Application of Column Extraction Method for Impurities Analysis on HB-Line Plutonium Oxide in Support of MOX Feed Product Specifications

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AA	Atomic Absorption
ADS	Analytical Development Section
AFS-2	Alternate Feedstocks 2
DF	Dilution Factor
EPA	Environmental Protection Agency
HP	High Purity
ICD	Interface Control Document
ICP-ES	Inductively Coupled Plasma - Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
IC	Ion Chromatography
IDL	Instrument Detection Level
IRL	Instrument Reporting Limit
MRL	Method Reporting Limit
MOX	Mixed Oxide
PPB	Parts-per-billion
PPT	Parts-per-trillion
RE	Rare Earth
SRNL	Savannah River National Laboratory

1.0 Introduction

The current mission at H-Canyon involves the dissolution of an Alternate Feedstocks 2 (AFS-2) inventory that contains plutonium metal. Once dissolved, HB-Line is tasked with purifying the plutonium solution via anion exchange, precipitating the Pu as oxalate, and calcining to form plutonium oxide (PuO_2). The PuO_2 will provide feed product for the Mixed Oxide (MOX) Fuel Fabrication Facility, and the anion exchange raffinate will be transferred to H-Canyon.[1,2]

The purity of the plutonium anion exchange product is essential for a successful MOX campaign. Consequently, HB-Line requests the development of an anion exchange flowsheet by the Savannah River National Laboratory (SRNL) that meets Interface Control Document (ICD) limits for the MOX Fuel Fabrication Facility (see Table 1-1).[3]   As noted in Table 1-1, the limits are divided into three columns; column B, column A, and exceptional, where column B lists the lowest required reporting limits in µg/g Pu for the elements of interest.

The SRNL Analytical Development section (ADS) is tasked with proving that reporting limits from their analytical methods meet these ICD limits for trace impurity levels.   Included on Table 1-1 are the preferred AD methods for each element, where a bulk of the analyses is from the Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) and Mass Spectrometry (ICP-MS) methods. The other method is Ion Chromatography (IC) for Cl and F. Most of the ICP-ES and ICP-MS analytes are routinely measured using guidance from technical procedures ADS-1543 for ICP-MS[4] and ADS-1573 for ICP-ES.[5] Ga and V, however, are not routinely measured on AD's ICP-MS method and required method development for the scope of this paper. Am and Np are semi-quantified on the ICP-MS. A method is not currently set up for Bi and In, as they are used as internal standards for the ICP-MS method.

It should be noted that the reporting limits are requested for loading tests of up to 80 g Pu/L.[1] Recent Pu measurements of the 13620B solution and January "Hearts Cut" sample submitted by the Separations and Actinides Science Program group respectively showed 45 g/L and 50 g/L Pu-239 on the ICP-MS method. The high Pu content in these samples imposes analytical matrix effects especially when performing a minimal dilution factor (DF) on ICP-ES and ICP-MS in an effort to meet the Column B limits.   These matrix effects are both spectral and non-spectral. In the case of ICP-ES, Pu emission lines cause spectral interferences on analytical wavelengths of interest, and for ICP-MS, Pu forms doubly-charged species at lower masses and isobaric spectral interferences on surrounding masses (e.g., U-238). While spectral matrix effects are corrective to some extent (but with difficulty) for both methods, the non-spectral effects are deleterious, since they are due to the high Pu present through the sample introduction system and ultimately in the plasma. In this instance, a high level of Pu from a low dilution factor in the plasma hinders the ICP's efficiency as an ion source for other analytes, especially when they are at trace levels. With the application of an internal standard, a significant suppression or enhancement in signal recovery is observed when compared with the calibration standards, subsequently diminishing the data quality and causing instrument drift.

Table 1-1. ICD Limits.

Chemical Component*	AD Method	B (μg/g Pu)	A (μg/g Pu)	Exceptional (μg/g Pu)
Al	ICP-ES	100	500	10000
B	ICP-ES	1	100	1000
Be	ICP-ES	100	100	2000
C	Not available	500	1000	5000
Ca	ICP-ES	150	500	10000
Cd	ICP-MS	5	10	1000
Cr	ICP-ES	200	1000	1500
Cu	ICP-ES	100	100	500
Fe	ICP-ES	500	2000	3000
Ga	ICP-MS	0.12	12000	12500
K	ICP-ES	100	300	10000
Li	ICP-ES	100	400	10000
Mg	ICP-ES	200	500	10000
Mn	ICP-ES	100	100	1000
Mo	ICP-MS	100	100	1000
Na	ICP-ES	100	1000	10000
Nb	ICP-MS	50	100	3500
Ni	ICP-ES	200	5000	12000
P	ICP-ES	250	200	1000
Pb	ICP-MS	100	200	1000
Si	ICP-ES	150	200	200
Sn	ICP-MS	100	100	2500
Ta	ICP-MS	200	200	500
Ti	ICP-ES	100	100	2500
U	ICP-MS	100	5000	Not provided
V	ICP-MS	5	300	2500
W	ICP-MS	100	200	2500
Zn	ICP-ES	100	150	1000
Zr	ICP-ES	50	50	1000
Gd	ICP-MS	0.5	3	250
F	IC	250	250	500
Cl	IC	250	250	500
Ag	ICP-MS	100	250	10000
Bi	Not set up	10	100	1000
Co	ICP-MS	50	100	10000
Dy	ICP-MS	0.5	1	1000
Eu	ICP-MS	0.5	1	1000
In	Not set up	20	20	1000
N	Not available	300	400	400
S	ICP-ES	250	250	1000
Sm	ICP-MS	2	2	1000
Th	ICP-MS	50	100	100
Np	ICP-MS	Not provided	500	Not provided
Am	ICP-MS	Not provided	7000	Not provided

*Elements that are analyzed on the ICP-ES method are listed for "ICP-ES," and elements analyzed on the ICP-MS method are listed for "ICP-MS."

The application of matrix-matched calibration standards or the method of standards addition can be used to address matrix effects. However, these approaches are not practical because of the extra accountability and safety measures needed to spike the standards with Pu. Furthermore, there are other consequences besides matrix effects when attempting to analyze samples with up to 80 g Pu/L with minimal dilution. An example is noted on the ICP-MS method, where Pu carryover in the sample introduction must be washed out with ~20% v/v HNO_3 sometimes requiring up to four hours. Another example is for ICP-ES, when the presence of potassium fluoride (KF) in these samples affects leaching of B and Si constituents from samples and reaction glassware, thereby skewing the B and Si measurements.

The purpose of this report is to detail an alternative analytical protocol from the typical sample dilution and analysis (i.e., "dilute and shoot") protocol on the ICP-ES and ICP-MS AD methods. With the application of Pu column extraction prior to analysis to eliminate the aforementioned matrix effects by removing the Pu, it is found that the HB-Line PuO_2 MOX Feed Product Specifications can be met. This alternate approach utilizes an Eichrom™ RE (Rare Earth) column for Pu removal, after which impurities analysis are performed on the elution product and raffinate. Due to the absence of Pu along with an amenable acid matrix, a significantly lower dilution factor (about two orders-of-magnitude lower) is accomplished on these sample types. The minimal dilution factor advertently drives down the method reporting limit (MRL) on the method, as shown:

$$MRL = IRL \times total\ DF.$$

The instrument reporting level (IRL) is multiplied by the total dilution factor, which is a combination of the sample dissolution dilution factor (or column extraction in this case) and instrument dilution factor. The IRL is derived from the instrument's detection limit (IDL) for a given analyte accordingly:

$$IRL = IDL \times 3.33.$$

As shown in the equation, the total dilution factor is directly proportional to the MRL, such that the lower dilution factors achievable as a result of Pu column removal help to reduce the MRL for an analyte, therefore ensuring that the ICD limits can be reached.

The IRL is the standard deviation of ten blank measurements on the ICP-ES multiplied by ten. On the ICP-MS method, the IRL is the average of the calibration blank and closing blank standard deviations multiplied by ten. The ICP-MS IRLs are calculated on a daily basis, whereas the ICP-ES IRLs are calculated at least annually. The ICP-MS determines a signal to noise ratio and transposes the number into an IRL with every use, and the ICP-ES does not and is periodically tested for detection levels. Environmental Protection Agency (EPA) method SW846 6010C (ICP-ES) states that the IDL should be established initially and then determined on an annual basis. The IRLs for most isotopes on the ICP-MS method are typically 10-ppt (parts-per-trillion), and it is found that the ICP-ES IRLs have remained relatively consistent at the lower parts-per-billion (ppb) levels for most elements. Consequently, the methods' IDLs were seen more as a constant during this method development for achieving lower MRLs, therefore placing all importance on the total dilution factor in the MRL equation.

Table 1-2 lists the analytical ICP-ES and ICP-MS IRLs and MRLs for the typical "dilute and shoot" protocol on a nominal 50 g/L Pu solution. For most elements on the preferred method (shaded in table 1-2), it is seen that the "dilute and shoot" protocol can be applied to meet the required limits. In some cases, the limits cannot be met (#'s in parenthesis). The Pu column

extraction method detailed in this report accomplishes those limits that cannot be attained by normal "dilute and shoot," since the samples can be analyzed at lower dilution factors.

Table 1-2. Analytical MRLs for "Dilute and Shoot" on Nominal 50 g/L Pu Solution.

element	Col A Standard limits µg/g Pu	Col B Desired limits µg/g Pu	preferred method		ICP-ES *MRL* (mg/L)	ICP-ES MRL µg/g Pu	ICP-MS *MRL* (mg/L)	ICP-MS MRL µg/g Pu
			ICP-ES	ICP-MS				
Ag	250	100		yes			0.25	5.0
Al	500	100	yes		0.28	5.6		
B	100	1	yes		0.66	(30)		
Be	100	100	yes		0.013	0.3		
Ca	500	150	yes		0.25	5.0		
Cd	10	5		yes			0.25	5.0
Co	100	50	yes		0.85	*17.0*		
Cr	1000	200	yes		0.82	16.4		
Cu	100	100	yes		0.63	12.6		
Dy	1	0.5		yes			1	(20)
Eu	1	0.5		yes			1	(20)
Fe	2000	500	yes		0.96	19.2		
Ga	12000	0.12		yes			1	(20)
Gd	3	0.5	yes	yes			1	(20)
K	300	100	yes		4.81	96.2		
Li	400	100	yes		0.23	4.7		
Mg	500	200	yes		0.15	3.0		
Mn	100	100	yes		0.21	4.3		
Mo	100	100	yes		0.99	19.7		
Na	1000	100	yes		0.33	6.6		
Nb	100	50		yes			0.25	5.0
Ni	5000	200	yes		1.6	32.0		
P	200	250	yes		1.39	27.8		
Pb	200	100		yes			0.25	5.0
S	250	250	yes		12.5	250		
Si	200	150	yes		1.56	31.2		
Sm	2	2		yes			1	(20)
Sn	100	100		yes			0.25	5.0
Ta	200	200		yes			0.25	5.0
Ti	100	100	yes		0.131	2.6		
Th	100	50		yes			0.25	5.0
V	300	5	yes		0.47	(9.4)		
W	200	100		yes			0.25	5.0
Zn	150	100	yes		0.919	18.4		
Zr	50	100		yes			0.25	5.0
U		100		yes			0.25	5.0

Parenthetical (#'s) did not meet column B limits

The following sections describe the experimental procedures for the sample column extraction, spiked sample column extraction, ICP-MS analysis, and ICP-ES analysis. The ICP-ES and ICP-MS results included in the report indicate that column extraction is a suitable method for meeting the ICD limits. Future work on both analytical methods and for other relevant matrices is recommended.

2.0 Experimental Procedure

2.1 Sample Column Extraction

Figure 2-1 shows the sample column extraction method. The steps are also described below:

1. 400-µL of ~50 g/L Pu "Hearts Cut" sample was diluted 12.5x with 4.4-mL 4 M HNO_3, 100-µL 4 M $NaNO_2$, and 100-µL 100 µg Nd tracer. The solution was loaded onto a double stack of Eichrom™ RE (Rare Earth) resin cartridges.
2. The raffinate was collected for ICP-ES and ICP-MS analysis of trace elements not retained on the columns. The raffinate sample dilution factor at this point was 12.5x.
3. 20-mL 3 M HCl was added to the columns to elute the retained trace elements off the columns.
4. The eluent was dried down to evaporate off the HCl and re-dissolved in 5-mL 0.1 M HNO_3 to provide a more suitable acid matrix for ICP-ES and ICP-MS analysis. The eluent sample dilution factor at this point was 12.5x.
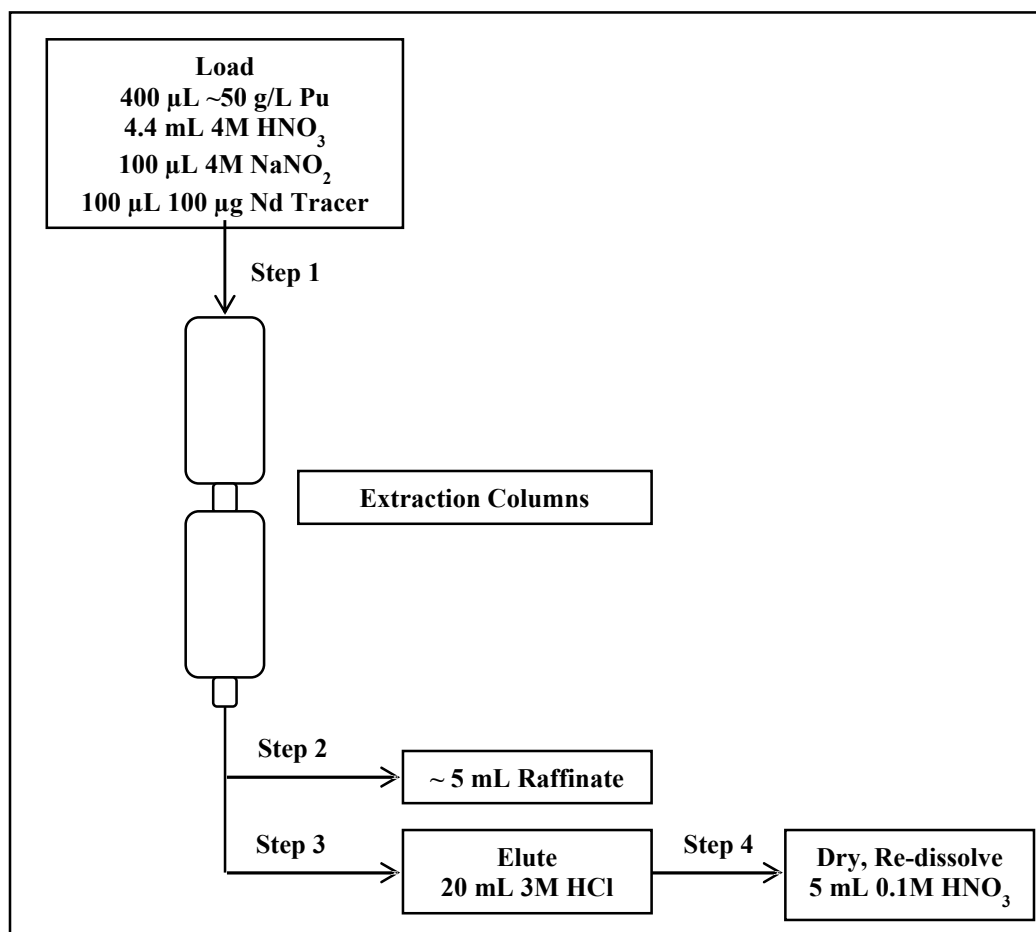

Figure 2-1. Sample Column Extraction.

2.2 Spiked Sample Column Extraction

To validate the efficiency of the method, an additional "Hearts Cut" aliquot was spiked with High Purity (HP) mixed standards. Figure 2-2 shows the extraction scheme, and the steps are described below:

1. 400-µL of ~50 g/L Pu "Hearts Cut" sample was diluted 12.5x with 4.3-mL 4 M HNO_3, 100-µL 4 M $NaNO_2$, and 100-µL 100 µg/mL each of High Purity Mix A and B standards. The solution was loaded onto a double stack of Eichrom™ RE (Rare Earth) resin cartridges. HP Mix A also contained Nd as the tracer.
2. The raffinate was collected for ICP-ES and ICP-MS analysis of trace elements not retained on the columns. The raffinate spiked sample dilution factor at this point was 12.5x.
3. 20-mL 3 M HCl was added to the columns to elute the retained trace elements off the columns.
4. The eluent was dried down to evaporate off the HCl and re-dissolved in 5-mL 0.1 M HNO_3 to provide a more suitable acid matrix for ICP-ES and ICP-MS analysis. The eluent spiked sample dilution factor at this point was 12.5x.
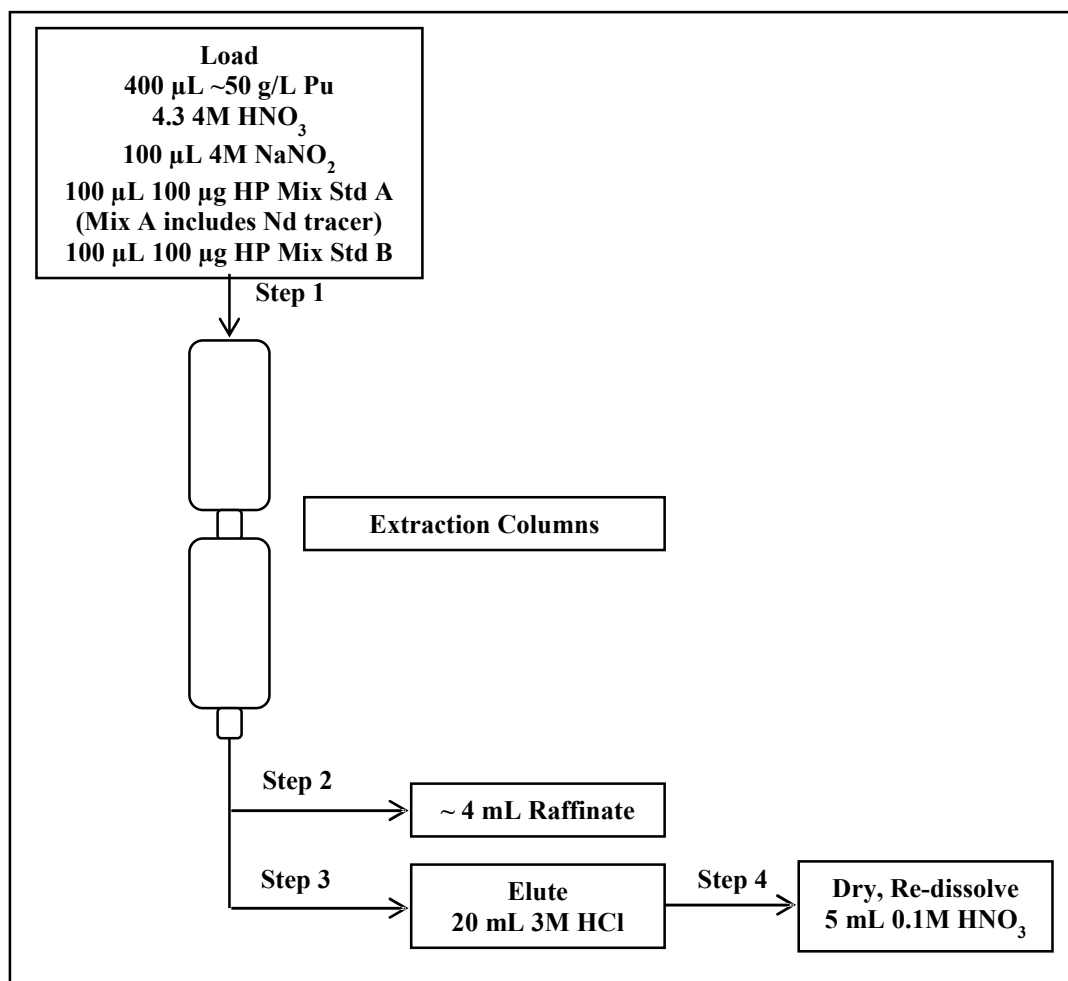

Figure 2-2. Spiked Sample Column Extraction.

Table 2-1 lists the elements along with the associated HP standard, either Mix A or Mix B. Also included is the collection step in which the element of interest was present, either in the raffinate or the eluent of the column extraction method. Some elements remained on the column and could not be analyzed, while others were observed in both the raffinate and eluent. ICP-ES and ICP-MS elements that are not in the standards but are listed on Table 1-1 are Am, Np, and S; these elements will be quantified without the extraction method.

Table 2-1. HP Standard Elements and Collection Steps

Element	HP Standard	Collection Step
Al	A	Raffinate/Eluent
B	A	Raffinate/Eluent
Be	A	Raffinate
Ca	A	Raffinate/Eluent
Cd	A	Raffinate
Cr	A	Raffinate
Cu	A	Raffinate
Fe	A	Eluent
Ga	A	Raffinate
K	A	Raffinate
Li	A	Raffinate
Mg	A	Raffinate/Eluent
Mn	A	Remained
Mo	B	Remained
Na	A	Raffinate
Nb	B	Remained
Ni	A	Raffinate
P	A	Raffinate/Eluent
Pb	A	Raffinate
Si	B	Raffinate
Sn	B	Raffinate
Ta	B	Remained
Ti	B	Eluent
U	A	Remained
V	A	Remained
W	B	Raffinate
Zn	A	Raffinate/Eluent
Zr	B	Remained
Gd	A	Eluent
Ag	B	Raffinate
Co	A	Raffinate
Dy	A	Eluent
Eu	A	Eluent
Sm	A	Eluent
Th	A	Remained

The purpose of the RE resin is not only to strip off the high Pu content for the raffinate, but also to elute off the trivalent, RE elements such as Sm, Eu, Gd, and Dy at a lower dilution factor, since they have significantly lower ICD limits (see Table 1-1). Studies show that the RE resin has an affinity for rare earths out of nitric acid solutions due to the nature of the resin's material, octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide (CMPO).[6] With the addition of 4 M $NaNO_2$ to oxidize the Pu to the 4+ state during the loading and the expectation from

experimental studies[6] that actinides are retained on the column, it should be noted that analysis of U, Th, Np, and Am are not feasible for this method. However, these components have higher ICD limits when compared to the rare earths and should be measurable without an extraction method.

2.3 ICP-MS Analysis

The sample raffinate, sample eluent, spiked sample raffinate, and spiked sample eluent were each analyzed in triplicate for quality control purposes on the Fisons Plasma Quad II ICP-MS instrument. The calibration curves consisted of blank, 1, 10, 25, and 50 ppb standards in 2% v/v HNO_3 with application of 25 ppb In and Bi internal standards. The ICP-MS method performed 2 acquisitions at 25 sweeps per acquisition for each standard and sample in the mass range of interest. The instrument dilution factors for the sample raffinate, sample eluent, spiked sample raffinate, and spiked sample eluent were respectively 10x, 20x, 100x, and 100x. For more detailed steps of the ICP-MS operation, see ADS-1543[4].

2.4 ICP-ES Analysis

Following ICP-MS analysis, the sample raffinate, sample eluent, spiked sample raffinate, and spiked sample eluent were analyzed on the Leeman Prodigy ICP-ES instrument. The calibration curves consisted of blank, blank, 5, and 10 ppm standards for most elements in 2% v/v HNO_3 with application of 2 ppm Sc internal standard. The ICP-ES method performed 3 integrations at 12 seconds per integration for each standard and sample on three different wavelengths per element. The instrument was set in radial mode. The instrument dilution factor was 2x except for the sample raffinate, which was 8x. For more detailed steps of the ICP-ES operation, see ADS-1573.[5]

3.0 Results and Discussion

The ICP-MS results in μg/g Pu of the raffinate and eluent are listed on Table 3-1. The results for each mass were corrected for natural isotopic abundance to yield an elemental concentration. Also included are the ICP-MS MRLs (calculated by dividing the isotope's MRL by the isotope's natural abundance) for these samples and the required ICD column B limits.[3] All results are based on an approximate concentration of 50 g/L Pu measured in a similar aliquot of the "Hearts Cut" sample. Additional masses for each element-of-interest where applicable are included to better validate the results. The HP Mix A and Mix B spike recoveries in the spiked raffinate and eluent are provided in the last column to show how well the column method worked, especially for the elution process. These spike recoveries are the true recoveries of the spiked elements from the spiked eluent sample and spiked raffinate sample, and are not corrected for the Nd tracer, which was also in HP Mix A.

Table 3-1. ICP-MS Results

Element	Isotope Used (m/z)	Avg. Elemental Result (μg/g Pu)	ICP-MS MRL (μg/g Pu)	ICD Col. B (μg/g Pu)	HP A & HP B Spike Recovery (%)
Cd	111	0.710	0.195	5	91
Cd	112	0.828	0.100	5	93
Cd	113	0.612	0.151	5	92
Cd	114	0.804	0.085	5	94
Ga	69	0.930	0.042	0.12	107
Ga	71	0.681	0.063	0.12	110
Pb	204	15.7	1.79	100	99
Pb	206	16.4	0.104	100	104
Pb	207	15.5	0.113	100	99
Pb	208	15.7	0.048	100	103
Sn	117	4.45	0.326	100	91
Sn	118	4.28	0.103	100	92
Sn	119	4.01	0.291	100	85
Sn	120	4.33	0.076	100	91
Co	59	0.369	0.025	50	105
Gd	155	9.31	0.169	0.5	55
Gd	156	9.66	0.122	0.5	54
Gd	157	9.05	0.159	0.5	56
Dy	163	0.403	0.100	0.5	55
Eu	151	0.077	0.052	0.5	54
Eu	153	0.119	0.048	0.5	54
Sm	147	0.424	0.167	2	54
Sm	149	0.218	0.181	2	55
Sm	152	0.292	0.093	2	56

In the case of the raffinate, the elements recovered in the 85 – 110% range. Most important is that while all results are positive, all masses have RLs that are below the required ICD limits for the raffinate due to the low dilution factor. While one purpose for this method was to attempt clean up a Pu sample for ICP-MS analysis of V in the raffinate, the method was unsuccessful since V remained on the column. Further attempts on the ICP-MS method should be made with the straight Pu "Hearts Cut" sample by ICP-MS for V.

The assessment of the rare earth elements (Gd, Dy, Eu, and Sm) in the eluent was imperative because of the low ICD requirements shown on Table 3-1. The HP Mix A and Mix B spike recoveries were approximately 50% as was also observed for the Nd tracer. Positive results were measured at the selected masses. It should be noted that higher recoveries could have been achieved, but this would have jeopardized the raffinate, in which the Ga required a minimal dilution factor. Table 3-2 shows the HP A and B spike recoveries after correcting for the Nd tracer, and all recoveries are within 94 – 98%. The Gd results are in agreement for the +/- 20% method, but the Eu and Sm results obviously show greater scatter. Nevertheless, these results along with the Dy-163 mass results are all below the required ICD limits. The ICP-MS MRLs at the low dilution factor show that the ICD limits are not exceeded.

Table 3-2. ICP-MS Results in the Eluent Corrected for Nd Tracer.

Element/Mass	HP A & HP B Spike Recovery (%) Nd Tracer Corrected
Gd-155	96
Gd-156	94
Gd-157	98
Dy-163	96
Eu-151	94
Eu-153	94
Sm-147	94
Sm-149	96
Sm-152	98

Table 3-3 lists the ICP-ES results in μg/g Pu of the raffinate and eluent. Also included are the calculated ICP-ES MRLs; the MRLs are the same for most elements since the actual results were not detectable. The last two columns list the ICD column B limits and HP Mix A and B spike recoveries. Analogous to the ICP-MS results, the results are based on an approximate concentration of 50 g/L Pu measured in a similar aliquot of the "Hearts Cut" sample.

Table 3-3. ICP-ES Results

Element	Result (μg/g Pu)	ICP-ES MRL (μg/g Pu)	ICD Col. B (μg/g Pu)	HP A & HP B Spike Recovery (%)
Be	< 1.60	1.60	100	97
Cd	< 6.20	6.20	5	93
Co	< 17.0	17.0	50	90
Cr	< 20.4	20.4	200	105
Cu	< 43.0	43.0	100	104
Fe	170	3.15	500	50
Gd	< 10.8	10.8	0.5	50
K	< 602	602	100	125
Li	< 29.2	29.2	100	100
Ni	<91.0	91.0	200	104
Pb	< 143	143	100	105
Sn	< 112	112	100	87
Ti	< 1.90	1.90	100	48

The raffinate MRLs are elevated since it was analyzed with an 8x instrument dilution factor, as there was limited sample volume. The HP Mix A and Mix B spike recoveries varied and were within 50 – 125%. In most cases the extracted analyte MRL's were lower than either ICD Column A or B limits. However, a majority of the limits may be achieved by routine dilute and shoot protocol. Several analyte limits were not achieved (e.g. Cd, Sn, Pb, and Gd) by either one or both protocols, and these elements will be analyzed by mass spectrometry. The potassium MRL, by extraction, exceeded both limits, and by dilute/shoot (see Table 1-2) is noted to be borderline for ICD Column B limit. Therefore, potassium may be performed by atomic absorption spectroscopy (AA) if needed. ICP-ES spike recoveries for HP Mix A and Mix B were similar to those run by ICP-MS.

4.0 Conclusions

The results presented in this report document the potential success of the RE resin column extraction application on highly concentrated Pu samples to meet MOX feed product specifications. The original "Hearts Cut" sample required a 10000x dilution to limit instrument drift on the ICP-MS method. The instrument dilution factors improved to 125x and 250x for the sample raffinate and sample eluent, respectively. As noted in the introduction, the significantly lower dilutions help to drop the total MRL for the analyte. Although the spike recoveries were half of expected in the eluent for several key elements, they were between 94 – 98% after Nd tracer correction. It is seen that the lower ICD limit requirements for the rare earths are attainable because of less dilution. Especially important is the extremely low Ga limit at 0.12 µg/g Pu; an ICP-MS method is now available to accomplish this task on the sample raffinate. While B and V meet the column A limits, further development is needed to meet the column B limits. Even though V remained on the RE resin column, an analysis method is ready for investigation on the ICP-MS, but it does not mean that V cannot be measured on the ICP-ES at a low dilution to meet the column B limits. Furthermore, this column method can be applicable for ICP-ES as shown in Table 3-2, in that it trims the sample of Pu, decreasing and sometimes eliminating Pu spectral interferences.

Table 4-1 summarizes AD methods targeting ICD column limits.

Table 4-1. Analytical summary methods to meet ICD limits (on nominal 50 g/L Pu solution).

Element	Col A limits µg/g Pu	Col B limits µg/g Pu	Preferred method (A=meets column A spec), (B=meets column B spec) (X = not meeting at this time)			
			ICP-ES	ICP-MS	ICP-MS (+column)	(text below)
Ag (Silver)	250	100		A,B		
Al (Aluminum)	500	100	A,B			
B (Boron)	100	1	A			
Be (Beryllium)	100	100	A,B			
Bi (Bismuth)	100	10				X
C (Carbon)	1000	500				X
Ca (Calcium)	500	150	A,B			
Cd (Cadmium)	10	5		A,B		
Cl (Chlorine)	250	250				X
Co (Cobalt)	100	50	A,B			
Cr (Chromium)	1000	200	A,B			
Cu (Copper)	100	100	A,B			
Dy (Dysprosium)	1	0.5			A,B	
Eu (Europium)	1	0.5			A,B	
F (Fluorine)	250	250				X
Fe (Iron)	2000	500	A,B			
Ga (Gallium)	12000	0.12			A,B	
Gd (Gadolinium)	3	0.5			A,B	
In (Indium)	20	20				X
K (Potassium)	300	100	A,B			
Li (Lithium)	400	100	A,B			
Mg (Magnesium)	500	200	A,B			
Mn (Manganese)	100	100	A,B			
Mo (Molybdenum)	100	100	A,B			
N (Nitrogen)	400	300				X
Na (Sodium)	1000	100	A,B			
Nb (Niobium)	100	50		A,B		
Ni (Nickel)	5000	200	A,B			
P (Phosphorus)	200	250	A,B			
Pb (Lead)	200	100		A,B		
S (Sulfur)	250	250	A,B			
Si (Silicon)	200	150	A,B			
Sm (Samarium)	2	2			A,B	
Sn (Tin)	100	100		A,B		
Ta (Tantalum)	200	200		A,B		
Ti (Titanium)	100	100	A,B			
Th (Thorium)	100	50		A,B		
V (Vanadium)	300	5	A			
W (Tungsten)	200	100		A,B		
Zn (Zinc)	150	100	A,B			
Zr (Zirconium)	50	100		A,B		
U (Uranium)		100		A,B		

Bi & In are ICP-MS internal standards

Cl & F to be analyzed in post calcined product

C & N by solids analyzer

B & V meet A spec, but not B spec, may need further development

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5.0 Recommendations for Future Work

The following recommendations are based upon results in this report.

- This data represents a single experiment for the application of the RE column extraction method. More work on this method is needed to validate the observations. This added testing also includes use of additional sample volumes for the ICP-ES method to better validate the application.
- The low limit for B (see Table 1-1) will require additional testing. Since B showed up in both the raffinate and eluent, either a method on the Plasma Quad II or Agilent 7700x ICP-MS instrument is needed for further evaluation.
- V remained on the RE column. Consequently, further testing on the straight "Hearts Cut" sample is recommended to ensure its limit is attainable on the ICP-ES. Also, method validation is suggested on the ICP-MS method.
- S was not tested during this application. The ICP-ES method proposes, based on previous testing, an instrument dilution factor at 16x on the straight "Hearts Cut" sample to meet the ICD limit.

6.0 References

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4. L.C. Johnson, "Inductively Coupled Plasma-Mass Spectrometer Elemental and Isotopic Analysis for Aqueous Liquid Samples PlasmaQuad II RADICPMS", ADS Procedure ADS-1543, Rev. 5.
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