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TITLE: **Analysis of TRU Waste for RCRA-Listed Elements**

AUTHOR(S): **Cynthia A. Mahan  
Dan Gerth  
Tom Yoshida  
Chris Bink**

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Author: Cynthia Mahan, CST 9, 5-3766.

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## ANALYSIS OF TRU WASTE FOR RCRA-LISTED ELEMENTS

Cynthia Mahan, Dan Gerth, Tom Yoshida, Chris Brink, Susan Pacheco,  
Michele Gross, Alex Martinez, Barbara Hemberger, Paula Cisneros, James Rodriguez  
Chemical Science and Technology, Inorganic Trace Analysis, CST 9  
Los Alamos National Laboratory, MS G740  
Los Alamos, NM 78745

### ABSTRACT

Analytical methods for RCRA listed elements on Portland cement type waste have been employed using both microwave and open hot plate digestions with subsequent analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), graphite furnace atomic absorption (GFAA) and cold vapor atomic absorption and fluorescence (CVAA/CVAFS). Four different digestion procedures were evaluated including an open hot plate nitric acid digestion, EPA SW-846 Method 3051, and 2 methods using modifications to Method 3051. The open hot plate and the modified Method 3051, which used aqua regia for dissolution, were the only methods which resulted in acceptable data quality for all 14 RCRA-listed elements. Results for the nitric acid open hot plate digestion were used to qualify the analytical methods for TRU waste characterization, and resulted in a 99% passing score.

Direct chemical analysis of TRU waste are being developed at Los Alamos National Laboratory in an attempt to circumvent the problems associated with strong acid digestion methods. Technology development includes laser induced breakdown spectroscopy (LIBS), laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS), dc arc CID atomic emission spectroscopy (DC-AES), and glow discharge mass spectrometry (GDMS). Analytical methods using the Portland cement matrix are currently being developed for each of the listed techniques. Upon completion of the development stage, blind samples will be distributed to each of the technology developers for RCRA metals characterization.

### I. INTRODUCTION

Transuranic waste (TRU) is defined as waste containing greater than 100 nanocuries of radioactivity per gram waste (for elements > 92 amu and half-lives of

greater than 20 years). TRU wastes were generated primarily from plutonium reprocessing and fabrication, research and development activities, environmental restoration, and decontamination and decommissioning activities throughout the DOE complex. DOE plans to dispose of approximately 175,600 cubic meters of TRU waste in the Waste Isolation Pilot Plant (WIPP) site.<sup>1</sup> Los Alamos National Laboratory (LANL) currently stores approximately 12,000 cubic meters of TRU waste (55,000 55-gallon drum equivalents). Hence, in order to fill the WIPP pipeline, LANL scientist are developing the capability to certify 3500-5500 drums/yr. of retrievable stored waste, in addition to the capability to characterize newly generated waste resulting from ongoing weapons activities. TRU waste characterization, including RCRA metal analysis is a primary component of compliance activities required to support the WIPP disposal activities. The Transuranic Waste Characterization Quality Assurance Program Plan (TWCP QAPP) describes the performance based requirements associated with TRU waste characterization. The New Mexico Environment Department (NMED) and the Environmental Protection Agency (EPA) Region VI, are responsible for enforcing RCRA regulations in the State of New Mexico. These regulatory agencies currently mandate the use of SW-846 methods for the characterization of RCRA constituents. All laboratories performing RCRA analysis on TRU waste that is destined for disposal at WIPP must qualify their analysis methods through the Performance Demonstration Program (PDP), administered by Idaho National Laboratory (INEL) in support of the TWCP program. LANL has participated in Cycles 1 and 2 of this demonstration program.

Several digestion methods have been investigated in this laboratory for the analysis of RCRA-listed metals on surrogate TRU waste forms. Scott, Brink, et. al., examined the effectiveness of EPA SW-846, Method 3051, a nitric acid microwave assisted digestion, using surrogates for pyrochemical salt and organic resin.<sup>2</sup> The results showed Pb recoveries of ca

60%, and Ag recoveries less than 25%. Subsequently, a modified method 3051 using an aqua regia mixture was developed and resulted in acceptable recoveries (> 90%) for the RCRA metals, including Pb and Ag. The modified 3051 method is the current digestion protocol used at LANL as well as other DOE facilities for the digestion of TRU material. The method was primarily developed for pyrochemical salts and organic resins. The performance on Portland cement type sample waste was not evaluated in the study. This procedure, along with an open hot plate nitric acid digestion, and microwave assisted nitric acid digestion (EPA SW-846 3051) method were evaluated using surrogate Portland cement samples obtained through INEL as part of the PDP. The analytical methods are discussed and results for the performance demonstration samples are presented.

Current methods of analysis used in the TWCP are costly, generate new waste as a result of the dissolution of the solid matrix, require considerable analytical resources to implement the associated QA program, and shorten the operational life expectancy of gloveboxes due to the strong acid concentrations used for sample digestions. Thus, analytical methods are needed that lower analysis cost, save time, minimize hazardous and mixed waste generation, and achieve regulatory compliance. LANL researchers are developing direct analysis techniques including laser induced breakdown spectroscopy (LIBS), laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS), dc arc CID atomic emission spectroscopy (DC-AES), and glow discharge mass spectrometry (GDMS), to characterize the TRU waste in the original solid form. A brief description of the direct chemical techniques and methods development activities are discussed.

## II. RCRA METAL ANALYSIS

Eight TRU sample surrogates for blind testing were received from INEL for the PDP Cycle 1. Four of the samples were in a Portland cement matrix and four samples were uncemented sludges (Type I Content Code 111/211). The surrogates were prepared by personnel at Argonne National Laboratory-East (ANL). The sludges were prepared by precipitating a solution containing matrix elements including Al, Ca and Fe, and the RCRA metals (i.e., Sb, As, Ba, Be, Cd, Cr, Pb, Hg, Ni, Se, Ag, Tl, V, and Zn). The precipitation was accomplished by raising the pH of the solution. The resultant precipitate constituted the sludge samples. A portion of the precipitate was mixed with Portland cement to produce the cemented samples.

### A. Open Hot Plate/Nitric Acid digestion

These samples were initially analyzed by an open hot plate HNO<sub>3</sub> digestion. The results were reported to INEL for Cycle 1 of the PDP. The procedure is similar to EPA SW-846 Method 3050 except that there is no peroxide addition. Half gram aliquants of the samples were weighed into 100 mL beakers. Ten milliliters of 1:1 nitric acid was added to each vessel and subsequently heated on a hot plate at ca 95°C for 30 min. Two additional 5 mL aliquots of 1:1 HNO<sub>3</sub> were added, the samples covered with watchglasses and refluxed for an additional 30 min. The solutions were taken to near dryness, followed by another 5 mL aliquot of 1:1 HNO<sub>3</sub>. The solutions were warmed on the hotplate to facilitate solubilization. Subsequently, the warmed samples were quantitatively transferred through acid washed 0.45 µm nalgene filters to remove the precipitated silica. Samples were diluted to 50 mL in the filter cups and swirled to render homogenous. The samples were then decanted into centrifuge tubes for analysis. All analyses were performed using the same digested solution.

A Thermo Jarrell Ash 61E emission spectrometer, Fisons PQ II ICP-MS, Perkin-Elmer 4100 graphite furnace and a Leeman Labs PS 200 Mercury Analyzer were used to measure element concentrations. A multi-instrument approach was used to measure the target analytes so that recoveries and detection limits could be assessed and aid in choosing the best technique for each analyte. Sb was measured by ICPMS; Hg was determined by CVAA and ICPMS; As, Be, Cd, Cr, Pb, Ni, Se, Ag, Tl, V and Zn were measured by ICPMS and ICPAES. As and Se were also measured by GFAA and Ba was analyzed by ICPAES.

Results for the cemented samples are shown in the following Tables. Results for As, Se and Hg have been combined under the column heading GF/CV, abbreviations for GFAA and CVAA. The values shown in the "known" column represent the concentrations of analyte added during the preparation of the samples, plus any background elements that were detected by the manufacturers. The values for %R were calculated by taking the analytical result and dividing by the 'known' concentrations and multiplying by 100. The values for %R were calculated for the techniques that are in the shaded boxes. The shaded boxes represent the actual values reported to INEL.

Element	Sample A (mg/kg)					Sample B (mg/kg)			
	ICPMS	ICPAES	GF/CV	Known	%R	ICPMS	ICPAES	GF/CV	Known
Sb	< 0.5			0	0	< 0.5			0
As	107	107	178	123	87	2.8	<10	2.4	0
Ba		1180		1187	99		38		0
Be	31	37		37	99	0.8	<1.0		0
Cd	15	17		19	91	<0.5	<2.0		0
Cr	125	153		164	93	27	28		0
Pb	97	113		115	99	2.2	6.9		0
Hg	1.0		4.2	4.2	101	<0.4		< 0.4	0
Ni	47	48		47	102	23	18		0
Se	14	< 10	13	18	74	0.7	< 10	< 1.0	0
Ag	11	13		24	55	<0.5	< 5		0
Tl	32	44		35	125	0.9	< 10		0
V	30	35		0	0	32	34		0
Zn	21	21		0	0	25	21		0

Element	Sample C (mg/kg)					Sample D (mg/kg)				
	ICPMS	ICPAES	GF/CV	Known	%R	ICPMS	ICPAES	GF/CV	%R	RPD
Sb	< 0.5				0.0	< 0.5			0	
As	40	34	52	40	101	39	37	50	98	2.5
Ba		250		266	94		240		90	4.1
Be	294	323		318	101	291	319		100	1.2
Cd	3.4	3.2		3.3	98	3.1	3.2		98	0
Cr	50	55		61.3	90	48	54		88	1.8
Pb	23	26		25	102	23	27		106	3.8
Hg	< 0.5		1.4	1.5	92	< 0.5		1.4	92	0
Ni	120	125		125	101	117	121		97	3.3
Se	4.7	< 10	< 1.0	3.9	120	3	< 10	< 1.0	76	44
Ag	126	141		157	90	123	141		90	0
Tl	18.1	25		21	120	17.8	26		125	4
V	31	36		0	0	29	34		0	6
Zn	20	21		0	0	20	21		0	0

There was good agreement between the known and the measured values for each technique on all 4 cemented samples. The accuracies, as measured by percent recoveries (%R) were generally between 90 and 100%. The data quality objectives that must be met for the TWCP stipulate recoveries within  $\pm 20\%$ , when the sample concentrations are  $\geq 10 \times \text{IDL}$  for ICPAES, and  $\geq 100 \times \text{IDL}$  for ICPMS. Although, the PDP scoring uses  $\pm 40\%R$ . All samples met the recovery requirements for all 14 RCRA-listed metals.

Some important observations can be made by comparing element results using different techniques. Hg was biased low for all three samples when measured by ICPMS. This problem was probably due to elevated background levels of Hg that were found in the blanks. The samples were blank-subtracted, resulting in lower Hg recoveries. Arsenic values were slightly higher

using GFAA relative to the ICPAES and ICPMS results. It appears there was some precipitation of Ag from the solutions as evidenced in the lower recoveries by both ICPMS and ICPAES. V and Zn seemed to be present in all the samples, including the matrix blank (Sample B), although this was not expected. Discussions with ANL personnel have confirmed that these elements were not added, nor were they analyzed, hence the "known" values were based on the premise that they were not a component of the precipitated sludge. Because the V and Zn concentrations were relatively consistent in all the cemented samples, and there was good agreement between the ICPMS and ICPAES results, it appears as though these elements were actually present in the samples. The concentration of V and Zn in all the uncemented sludges were ca 7 and 2 mg/kg, respectively. Therefore, the contamination is likely present in the Portland cement matrix. Cr and

Ni were also detected in the matrix blank. They also appear to be a constituent in the Portland cement matrix as the uncemented sludge sample blank was found to contain < 5 mg/kg of both elements. In terms of PDP scoring, there is no penalty for reporting false positives unless they are found in concentrations greater than 50% of the PRQL.

Although unknown at the time of analysis, Samples C and D were duplicates. The relative percent differences (RPD) between the results of the duplicate samples for the same techniques were < 6% for all the elements, except Se. The low concentration of Se present in the sample resulted in a 44% RPD. RPD is calculated using the formula

$$RPD = |C_xS1 - C_xS2| / ((C_xS1 + C_xS2) / 2)$$

Sample A (mg/kg)										
Element	Known	PRQL	Original	Added	MS	%R	Added	MSD	%R	RPD
			Result	Conc	Result		Conc	Result		
Sb	0	100	< 0.5	94	77	82	97	73	78	5.3
As	123	100	107	94	198	97	97	187	85	5.7
Ba	1187	2000	1180	1874	3132	104	1949	3100	103	1.0
Be	37	100	37	94	123	92	97	127	96	3.2
Cd	19	20	17	19	34	90	19	33	84	3.3
Cr	164	100	153	94	244	97	97	236	88	3.3
Pb	115	100	113	94	200	93	97	196	88	2.0
Hg	4	4	4.2	3.8	8.4	111	3.9	8.3	108	1.2
Ni	47	100	48	94	133	90	97	131	88	1.5
Se	18	20	14	19	30	87	19	31	92	3.3
Ag	24	100	13	94	99	92	97	97	89	2.0
Tl	35	100	44	94	135	97	97	124	85	8.5
V	0	100	35	94	125	96	97	122	93	2.4
Zn	0	100	21	94	107	92	97	104	88	2.8

MS and MSD recoveries were calculated according to the formula

$$\%R = (C_xS_p - C_xS_o) / C_A * 100$$

where  $C_xS_o$  represents the measured concentration of the unspiked sample (mg/kg),  $C_xS_p$  is the measured concentration of the spiked sample (mg/kg), and  $C_A$  is the concentration of the added spike (mg/kg). The recoveries for both the MS and the MSD were within the  $\pm 20\%$  limits for both the PDP scoring and the QAPP. In addition, the RPDs are much less than the required criteria of  $\leq 30\%$ . Also, the V and Zn recoveries provide additional evidence for the presence of these elements in the original cemented samples.

where  $C_x$  is the concentration of Sample 1 (S1) or duplicate Sample (S2). The data quality objective for duplicate blinds is that the RPD must be  $\leq 30\%$  when sample concentrations are  $\geq 10 \times$  IDL for ICPAES, and  $\geq 100 \times$  IDL for ICPMS. Thus, the DQOs were also exceeded for all target analytes for the duplicate blind samples.

The QAPP that governs the TWCP also specifies the determination of matrix spikes (MS) and matrix spike duplicates (MSD). These quality control samples help determine the reproducibility of the analysis and assists in the identification of matrix interferences. One sample in each analytical batch is spiked in duplicate with all the RCRA metals at the Program Required Quantitation Limits (PRQLs). Recoveries of these spiked samples are shown in the following Table.

The open hot plate nitric acid digestion proved to be an excellent method for all 14 RCRA metals in the Portland cement and uncemented sludges. Analytical results for the uncemented samples were similar to the results for the cemented samples, but are not shown in this article due to the need for brevity. Results show excellent accuracy and reproducibility for the majority of elements, regardless of the technique used, except in the case of Hg. Obviously, the preferred instrumental technique must be based on whether the target analytes meet the program required detection limits (PRDLs). The PRDLs are 100  $\mu\text{g/L}$  for all metals, except Cd and Se are 20  $\mu\text{g/L}$ , Ba is 2000  $\mu\text{g/L}$ , and Hg is 4.0  $\mu\text{g/L}$ . In addition, ICPAES is preferred over ICPMS when the performance is comparable. Although, several analytical techniques could have been qualified through

the PDP, only CVAA for Hg; ICPMS for Sb, As and Se; and ICPAES for Ba, Be, Cd, Cr, Pb, Ni, Ag, Tl, V and Zn were reported to the Program. Actually, ICPAES met the PRDLs for all the elements except Hg and Sb. However, prior experience measuring As and Se by emission led to the decision to use ICPMS as the preferred technique. As and Se could also have been qualified by GFAA, but our laboratory does not have a working glove-box instrument for the analysis of real TRU wastes.

Although, the hot plate digestion was more than satisfactory, the TRU Waste Program is structured on employing microwave assisted digestion as the sample preparation method for TRU wastes. Hence, EPA SW-846 method 3051 was tested on the same samples to compare the performance.

#### B. EPA SW-846 METHOD 3051

EPA SW-846 Method 3051 was tested by Scott on other TRU surrogates, but the effectiveness on Portland cements was not assessed. The preferred digestion method for TRU samples would avoid the use of hydrochloric acid, due to its corrosive nature on both glove boxes and analytical instrumentation. Also, formation of  $\text{ArCl}^+$  ions interferes with the monoisotopic measurement of As at 75 amu. Hence, it was important to evaluate a simple nitric acid digestion procedure.

A CEM MDS 2000 temperature and pressure controlled microwave digestion system was used for these studies. A 0.5 g aliquant of the sample was weighed into microwave digestion vessels. Ten milliliters of concentrated nitric acid was added to each vessel. The samples were microwaved at a pressure of 60 psi for 10 minutes. Temperatures reached 160°C in the control vessels. The cooled samples were quantitatively transferred through 0.45  $\mu\text{m}$  nalgene filters. Samples were diluted to 50 mL in the filter cups and swirled to render homogenous. The samples were then decanted into centrifuge tubes for analysis. All analysis were performed using the same digested solution.

This analysis was performed in a radiological controlled facility in anticipation of the need to analyze

real wastes. The prior analysis was achieved in a non-radiological facility due to the availability of instrumentation coupled with the strict turnaround time required. The new instrumentation used in the analysis included a VG Plasma Quad II, a Thermo-Jarrell Ash IRIS ICPAES, and a PS Analytical Merlin Hg Analyzer.

Low recoveries for Sb (20%) and Ag (<10%) were obtained for the MS and MSD. Ag was not detected in samples A and C which had known concentrations of 115 and 157 mg/kg, respectively. Pb recoveries by ICPMS were excellent (90-100%) for the PDP samples, as well as the MS and MSD. Pb measurement using the IRIS resulted in higher than expected detection limits. The Pb 220.4 nm line is located on the shoulder of an intense Al line, which is the cause of the lower sensitivity. The other 11 target analytes met all the DQOs.

Prior to using the high concentration HCl modified MW digestion method developed by Scott, a more benign aqua regia mixture using 1:3 HCl:HNO<sub>3</sub> was tested. The same microwave procedure described in the preceding paragraph was used except that 7.5 mL of concentrated nitric acid and 2.5 mL of concentrated hydrochloric acid were added to each vessel. Antimony recoveries improved slightly to 38% with the addition of HCl, whereas Ag still precipitated from both the unspiked samples as well as the spiked samples.

#### C. MODIFIED EPA SW-846 3051

Efforts to minimize the use of high concentrations of HCl in the preparation of samples did not succeed. Hence, the PDP samples were digested using the modified 3051 method, developed by Scott. The same preparation steps described in section B were used in this study, except 2 mL of concentrated nitric acid and 7.5 mL of concentrated hydrochloric acid were added to each vessel. The samples were microwaved at a pressure of 60 psi for 10 minutes with temperatures reaching 160°C in the control vessel.

Results on the 4 Portland cement samples are shown in the following Table. The CVAFS results for Hg are combined in the column labeled ICPAES/CV.



Element	Sample A (mg/kg)				Sample B (mg/kg)		
	ICPMS	ICPAES/CV	Known	%R	ICPMS	ICPAES/CV	Known
Sb	1		0		1		0
As	145		123	118	6		0
Ba		1297	1187	109		42	0
Be	43	38	37	103	< 3	0.6	0
Cd	20	29	19	153	1	2.0	0
Cr	185	188	164	115	46	32	0
Pb	120	63	115	104	7	< 20	0
Hg		4	4			< 0.1	0
Ni	66	66	47	140	31	32	0
Se	21		18		< 6		0
Ag	18	14	24	58	< 2	< 4	0
Tl	37		35	106	< 0.5		0
V	45	40	0		34	39	0
Zn	30	29	0		41	34	0

Element	Sample C (mg/kg)				Sample D (mg/kg)			
	ICPMS	ICPAES/CV	Known	%R	ICPMS	ICPAES/CV	%R	%RPD
Sb	< 1				< 1			
As	44		40	110	52		130	17
Ba		237	266	89		267	100	12
Be	315	298	318	94	360	339	107	13
Cd	4	7.2	3.3	218	4	7.6	121	5.4
Cr	63	57	61	93	71	63	103	10
Pb	24	< 20	25	96	27	< 20	108	12
Hg		1.5	1.5			1.5		
Ni	135	140	125	112	145	161	129	14
Se	< 6		3.9		< 6			
Ag	170	166	157	106	140	148	94	12
Tl	18		21	86	20		95	11
V	31	31	0		49	35		
Zn	29	25	0		30	27		

The recoveries for most elements were generally higher than the results obtained with the open hot plate digestion method. Ni recovery on Sample A for both ICPMS and ICPAES was 140%, and for Samples C and D were 112% and 129%, respectively. The high concentrations suggest a contamination problem. As was also biased high for all 4 samples. The problem may be an under correction for the isotopic interference of ArCl<sup>+</sup> at mass 75. Cd was biased high for all samples, although in Sample A there was good recovery, and the concentrations in Samples C and D were below the PRQL of 20 mg/kg. Pb concentrations by ICPMS were near the expected values, whereas the emission values were biased low. The Pb problem was identified and discussed in the previous section. Future

TRU waste analysis of Pb will be performed using ICPMS.

### III. CONCLUSIONS

Standard EPA SW-846 Method 3051 microwave assisted nitric acid digestion resulted in low recoveries for Sb, and Ag. Modified method 3051 using 3:1 HCl/HNO<sub>3</sub> solution, and the open hot plate nitric acid digestion showed comparable performance using surrogate samples comprised of a Portland cement matrix. However, a potential Ni contamination was discovered using the microwave assisted digestion. This problem will require resolution before the DQOs can be met for the TRU program. Also, As determinations appear to suffer from a matrix interference due to the

high concentration of chloride present in the digests. There was generally less precision in the MW method as evidenced by recoveries and RPD for the MS and MSD. The modified method which was shown to work well on pyrochemical salts and organic resins was also a sufficient digestion procedure for Portland cement, although some minor methods modification will be required.

The PDP scoring for all 8 cemented and uncemented blind samples resulted in 307 points out of a possible 309 points (99%). The only deficiency was an under-recovery of Sb (78%) on one of the MS samples.

#### IV. TECHNOLOGY DEVELOPMENT: DIRECT CHEMICAL ANALYSIS

Los Alamos is home to The Center for Direct Chemical Analysis (CDCA). A virtual center whose purpose is to develop, improve and apply direct measurement techniques to a variety of analytical problems. Direct chemical analysis measures the analytes directly in the solid material with minimal sample pretreatment. Conventional techniques such as atomic absorption and emission spectroscopy require that the solid materials be rendered in aqueous solution using concentrated acids prior to measurement. Thus, direct chemical analysis completely bypasses the digestion process, thereby increasing the sample throughput, saving both time and money.

Direct chemical methods to characterize TRU waste that are currently under development at the Center, (but are not approved for TRU waste characterization) include laser induced breakdown spectroscopy (LIBS), laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS), dc arc CID atomic emission spectroscopy (DC-AES), and glow discharge mass spectrometry (GDMS). Advantages of these direct chemical analysis methods include rapid analysis turnaround times, reduced cost, no additional mixed-wastes generated as a consequence of sample pretreatment, reduction of worker exposure to harmful reagents and radioactive samples, and decreased risk of sample contamination and analyte loss. In addition, LIBS can be performed *in situ*.

Analytical methods using the Portland cement matrix are currently being developed for each of the listed techniques. Upon completion of the development stage, blind samples will be distributed to each of the technology developers for RCRA metals characterization. The round-robin testing will help determine which technique(s) hold the most promise for

TRU characterization. The most promising technique(s) will continue development including, glove box installations, re-engineering for mobile platforms if applicable, and placement into service. The technology is briefly described in the following paragraphs.

DC-AES is a bulk solids analytical technique which uses a solid state integrating detector to measure the spectral emission intensities produced when a sample is vaporized and excited by a dc arc. The CID detector represents relatively new technology which has the potential to improve analytical performance over the traditional dc arc and conventional spectroscopic techniques. Samples are pulverized, mixed with graphite powder, and burned in the lower of two vertically mounted graphite electrodes. The detector chip is similar to a photographic plate in that it provides for continuous wavelength coverage and hence most elements in the periodic table can be determined if present in sufficient quantity. Potential analytical benefits over conventional spectroscopic methods include full elemental fingerprinting of the sample, the ability to detect weak spectral lines in the midst of strong matrix signals, improved sample throughput, simultaneous background correction, minimal sample preparation, and instrumental ruggedness.

LA-ICPMS uses a focused laser beam to ablate nanogram to microgram amounts of a sample into the plasma. The ablated material is transported by a stream of argon into the ICP-MS where the material is vaporized, dissociated and ionized. A pellet is formed from the sample after the addition of cellulose. The laser (neodymium YAG laser, 266 nm) is rastered across the surface of the pellet. Two methods of signal normalization are currently under investigation. The first method involves adding a liquid phase internal standard to the samples prior to analysis. The sample is subsequently dried and pressed into a pellet. The second method for signal normalization relies on particle counting. Instead of internal standard addition, a portion of the ablated particle stream is diverted into a particle counter. Analyte calibration is accomplished using standard addition. The standard can be added to the powder samples prior to analysis or during the analysis. Results of these standard addition and calibration experiments on TRU waste forms will be presented.

In the LIBS method, laser pulses are focused on the sample to generate a microplasma. The spectral emission from this plasma is measured to determine element concentrations. Initial results show excellent quantitative information for some elements. A LIBS instrument is in the process of being installed in a

glove-box and results on actual TRU waste are expected this summer. Preliminary data will be presented.

Glow discharge mass spectrometry (GDMS) is a direct sputtering analytical technique, wherein the surface of an electrically conducting sample is bombarded by  $\text{Ar}^+$  ions. Sputtered sample atoms are ionized separately, via interactions with  $\text{Ar}^*$  metastables. The separation of atomization from ionization greatly reduces matrix dependency, and permits a wide range of standardization schemes for quantitative analysis. The GDMS can perform rapid quantitative major element analysis (weight % level) and trace analysis to the sub-ppb level in a single run by using multiple detection systems (Faraday cup, and post-acceleration detector operable in both analogue and ion-counting mode). The double focusing geometry and magnetic sector permit routine operation at resolutions  $> 4000$ . Non-conducting powders must be combined with a high-purity ( $>99.995\%$ ) conducting metal powder (usually Ta), homogenized, and analyzed as a composite. Samples are baked in vacuo, pre-sputtered for 30 minutes, and quantitatively analyzed. Advantages of GDMS analysis include its high resolution (up to  $\text{DM}/\text{M}=12,000$ ) capabilities, its ability to acquire quantitative data for all RCRA metals (and nearly all elements in the periodic table), and its wide ( $>10^9$ ) dynamic range. Matrix-matching is not required

by GDMS. Standardization is easily accomplished through the use of both NIST standard reference materials (metals, ceramics and geological materials), and carefully prepared mixes of high-purity metal and metal oxide powders. Results of quantitative analyses of TRU waste surrogates by GDMS, and progress on instrument modifications and glove box installation will be discussed.

#### ACKNOWLEDGMENTS

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