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FUELS\*

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# MEASUREMENT TECHNIQUES IN DRY-POWDERED PROCESSING OF SPENT NUCLEAR FUELS

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## ABSTRACT

High-performance liquid chromatography (HPLC) with inductively coupled plasma mass spectrometry (ICPMS) detection,  $\alpha$ -spectrometry ( $\alpha$ -S), and  $\gamma$ -spectrometry ( $\gamma$ -S) were used for the determination of nuclide content in five samples excised from a high-burnup fuel rod taken from a pressurized water reactor (PWR). The samples were prepared for analysis by dissolution of dry-powdered samples. The measurement techniques required no separation of the plutonium, uranium, and fission products. The sample preparation and analysis techniques showed promise for in-line analysis of highly-irradiated spent fuels in a dry-powdered process. The analytical results allowed the determination of fuel burnup based on  $^{148}\text{Nd}$ , Pu, and U content. A goal of this effort is to develop the HPLC-ICPMS method for direct fissile material accountancy in the dry-powdered processing of spent nuclear fuel.

## INTRODUCTION

The objective of this work is to develop a dry-powdered processing method along with a HPLC-ICPMS technique for the determination of the content of 31 nuclides in five samples excised from a single fuel rod. The complete analysis of these samples includes the determination of the nuclides  $^{95}\text{Mo}$ ,  $^{99}\text{Tc}$ ,  $^{101}\text{Ru}$ ,  $^{103}\text{Rh}$ ,  $^{109}\text{Ag}$ ,  $^{137}\text{Cs}$ ,  $^{143}\text{Nd}$ ,  $^{145}\text{Nd}$ ,  $^{148}\text{Nd}$ ,  $^{147}\text{Sm}$ ,  $^{149}\text{Sm}$ ,  $^{150}\text{Sm}$ ,  $^{151}\text{Sm}$ ,  $^{152}\text{Sm}$ ,  $^{151}\text{Eu}$ ,  $^{153}\text{Eu}$ ,  $^{155}\text{Eu}$ ,  $^{155}\text{Gd}$ ,  $^{234}\text{U}$ ,  $^{235}\text{U}$ ,  $^{236}\text{U}$ ,  $^{238}\text{U}$ ,  $^{237}\text{Np}$ ,  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{241}\text{Pu}$ ,  $^{242}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{242\text{m}}\text{Am}$ , and  $^{243}\text{Am}$ . These analyses will provide the information necessary for the calculation of atom percent fission (fuel burnup) based on  $^{148}\text{Nd}$ , Pu, and U content [1] and for accountancy of fissile nuclear material for each sample. Additionally, replicate analyses of multiple samples will allow us to assess the precision of the HPLC-ICPMS method and the heterogeneity of the fuel.

## BACKGROUND

Proposed alternative fuel-cycle concepts involve the recycle of spent fuel without the separation of plutonium, uranium, and fission products. The nonproliferation advantages that are usually associated with the concepts are: (a) the highly radioactive spent fuel presents a barrier to the physical diversion of the nuclear material from the fuel cycle; and (b) there is no need to dissolve and chemically separate the plutonium, uranium, and fission products. Although high radiation levels and non-separation processing may be perceived as barriers to terrorists or other sub-national groups, concerns over international proliferation are primarily being addressed by direct material accountancy and verification, which are the international safeguard measures of fundamental importance. Consequently, the non-separation fuel cycle concepts have to be evaluated on the basis of the impact that the fuel cycle processes may have on direct nuclear materials accountancy. The Argonne experience with direct nuclear material accountancy has emphasized the need to develop destructive analysis (DA) methods for non-separated spent fuels with high-burnup [2]. By "direct accountancy" is meant direct measurement of the plutonium content in the fuel as compared to the indirect measurement by non-destructive assay (NDA) of a progeny product (e.g.,  $^{243}\text{Cm}$ ) from which the plutonium content is inferred. The progeny component exacerbates the accuracy and reliability of the plutonium content determination. Safeguards R&D must address the implementation of DA and NDA methods for flow and inventory operational control in dry bulk powdered processing.

The Korea Atomic Energy Research Institute (KAERI) has developed an advanced fuel cycle concept (DUPIC, direct use of spent PWR fuel) that utilizes dry-bulk processing techniques with no separation of plutonium/uranium/fission products. The dry-powdered process involves the mechanical dismantling, segmenting, and decladding of the PWR fuel elements, then pulverizing the  $UO_2/PuO_2$  spent fuel into powder. The spent fuel oxide powder is then subjected to cycles of oxidation/reduction, sintered into pellets, and configured into CANDU fuel bundles.

We are investigating nuclide measurement methods for highly irradiated spent fuels from the Three Mile Island (TMI) PWRs (45-50 GWd/MTU). The DA measurements are performed on aliquot samplings from the bulk dry-powdered spent fuel. The measurement techniques require no separation of the plutonium/uranium/fission products in the fuel element segments.

## MATERIALS AND METHODS

We have analyzed five samples from fuel rods with maximum burnups ~50 GWd/MTU originating from the TMI-1 reactor. The five samples analyzed in this work are listed in Table 1. These fuel samples were cut from fuel rod segments provided by GE-VNC. Table 1 lists the sample designations, the location in the fuel rod segment from which the individual samples were excised, and the sample size. The fuel rod used in this work is a  $UO_2$  fuel with an initial 4.0%  $^{235}U$  enrichment that was irradiated in TMI-1 PWR. Five samples (TMI A2, TMI B2, TMI C1, TMI C3, and TMI D2) that were cut from four individual segments were analyzed. These segments range in length from 30 to 33 in. and constitute the middle two-thirds of the approximately 15-ft long rod. The rod segments are thought to have a fairly uniform burnup of ~50 GWd/MTU [3].

Table 1. Spent nuclear fuel samples analyzed, mass of clad samples, and mass of declad fuel recovered from homogenization.

Fuel Rod Number	ANLCMT Sample ID	Location LEP, in.	Sample Length, in.	Clad Sample Mass, g	Homogenized Fuel Recovered Mass, g
TMI/I05243	TMI A2	29.4	0.56	11.11	8.16
TMI/I05243	TMI B2	45.3	0.41	8.06	6.27
TMI/I05243	TMI C1	92.7	0.50	8.78	6.95
TMI/I05243	TMI C3	61.5	0.50	9.52	6.48
TMI/I05243	TMI D2	126.8	0.50	6.76	5.03

The five samples were cut from their respective fuel rod segments. Preparation for analysis consisted of unloading the cut samples from the storage cask, identifying the fuel sample, and separating the fuel meat from the cladding. The fuel meat was separated from the cladding by use of a Plattner's diamond mortar modified with a 1-m long sleeve and a 2-kg tool steel pestle. In each case, all of the fuel fragments were recovered from the mortar and further crushed and homogenized with a Wig-L-Bug shaker in hardened tool steel vials and ball pestle. A new vial and ball pestle were used with each sample to minimize cross-contamination. The powdered fuel was stored in glass vials and reserved for analysis. This method of analytical fuel sampling has been demonstrated to provide excellent sample homogeneity, <1.5% relative standard deviation (RSD) for multiple aliquots, with respect to U and Pu content in homogenized powdered samples of PWR fuels with burnups in the range of 18-64 GWd/MTU [4].

A 0.1- to 0.2-g aliquot of the homogenized fuel sample powder was taken for dissolution and analysis. The powdered samples were dissolved in Parr Bomb vessels with Teflon liners. The fuel was added to a weighed Teflon liner. A new liner was used for each sample. The liner was

reweighed, and a mixture of  $\text{HNO}_3$ - $\text{HCl}$ - $\text{HF}$  was added to the liner. The Parr bomb was assembled and placed in a  $150^\circ\text{C}$  oven for 20 h and allowed to cool for 2 h. The vessel was opened, and the solution was examined. In all cases, the dissolution produced a yellow and translucent solution, indicating that the dissolution was complete. The solution was quantitatively transferred to a low-density polyethylene wash bottle that had been weighed. The Teflon® liner was triply rinsed with 2 M  $\text{HNO}_3$ , and the rinse solutions were combined with the initial dissolution solution. The wash bottle was reweighed, and the total mass of solution was determined by a difference calculation. The final dissolved fuel solution weighed approximately 50-g.

A working solution for analysis was prepared by diluting approximately 1 g of the dissolved fuel solution to 100 mL. Solution analyses were performed with ICPMS,  $\gamma$ -S, and  $\alpha$ -S. Table 2 lists the nuclides analyzed along with the analytical and calibration method used. The  $^{238}\text{U}$  concentration was determined on a solution diluted 100-fold from the working solution. Two independent calibration methods were used: (1) internal standardization with  $^{209}\text{Bi}$  and external calibration via linear regression using a commercially available  $^{238}\text{U}$  standard (SPEX Industries) and (2) isotope dilution with a  $^{233}\text{U}$  spike (New Brunswick Laboratory CRM 111A). The concentrations of  $^{241}\text{Am}$ ,  $^{137}\text{Cs}$ , and  $^{155}\text{Eu}$  were determined by direct  $\gamma$ -S analysis of a 5-mL aliquot of the 100-fold diluted sample using a  $\gamma$ -spectrometer with a known response determined with a multiradionuclide external standard (ES).

Nuclides free of isobaric interferences were determined directly in the working solution with ICPMS. Internal standardization was done with  $^{115}\text{In}$  and  $^{209}\text{Bi}$ . External calibration involved linear regression of data obtained using commercially available multi-element standards (SPEX Industries) with known natural abundance isotopic content. Ruthenium-99 was used as a surrogate calibration element for  $^{99}\text{Tc}$  in the standard solutions.

Several nuclides could not be determined directly with ICPMS due to significant isobaric interferences. As a result, analysis of these nuclides required chemical separation of interfering species. Chemical separations and analysis of Nd, Pm, Sm, Eu, and Gd were performed by use of HPLC-ICPMS. The relative isotopic abundance of individual isotopes of each element was measured by isotope ratio (IR) determination with ICPMS. The absolute concentration of each isotope could then be calculated relative to the absolute concentration of an isobar-free nuclide, as determined from direct ICPMS analysis. Samarium-152 was the benchmark nuclide for Sm isotopes. Europium-153 was the benchmark nuclide for Eu isotopes. Gadolinium-156 was the benchmark for Gd isotopes. Neodymium isotopes were determined by isotope dilution (ID) with a  $^{150}\text{Nd}$  isotopic spike (provided by ANL Analytical Chemistry Laboratory) for definitive results.

Minor uranium isotopes,  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{243}\text{Am}$  were determined by direct ICPMS analysis of the working solution using the ID method with a  $^{233}\text{U}$  isotopic spike. Other actinides were determined in chemically separated aliquots of the working solution. Actinide elements were chemically separated by ion exchange chromatography, providing Pu fractions and Am fractions for analyses of individual isotopes of each element. All plutonium isotopes except  $^{238}\text{Pu}$  were determined by the ID method with a  $^{244}\text{Pu}$  isotopic spike (National Bureau of Standards SRM 996), including a reanalysis of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ . Plutonium-239 and -240 were determined by two independent methods. Plutonium-238 was determined by  $\alpha$ -S using the mean  $^{239}\text{Pu}/^{240}\text{Pu}$  mass ratio that had been determined by direct analysis of the dissolved fuel with ICPMS in the separated Pu fraction. This ratio was converted to total  $^{239}\text{Pu}+^{240}\text{Pu}$  activity, and the  $^{239}\text{Pu}+^{240}\text{Pu}$  composite peak was used as a benchmark for the determination of  $^{238}\text{Pu}$  by  $\alpha$ -S. The isotopic composition of Am was determined from the isotopic ratio measured by ICPMS of the chemically separated Am fraction. These ratios were corrected for the presence of small amounts of  $^{242}\text{Pu}$  in the Am fraction due to incomplete radiochemical separation of the two elements. The concentration of  $^{242\text{m}}\text{Am}$  was calculated using  $^{241}\text{Am}$ , a nuclide determined with  $\gamma$ -S, as a benchmark.

Table 2. Analytical techniques and calibration methods for nuclides determined in this work.

Nuclide	Technique(s)	Calibration Method(s)
<sup>95</sup> Mo	ICPMS	LR
<sup>99</sup> Tc	ICPMS	LR
<sup>101</sup> Ru	ICPMS	LR
<sup>103</sup> Rh	ICPMS	LR
<sup>109</sup> Ag	ICPMS	LR
<sup>137</sup> Cs	γ-S	ES
<sup>143</sup> Nd	ICPMS	LR, ID
<sup>145</sup> Nd	ICPMS	LR, ID
<sup>148</sup> Nd	HPLC-ICPMS	ID
<sup>147</sup> Sm	HPLC-ICPMS	RD
<sup>149</sup> Sm	ICPMS	LR, ID
<sup>150</sup> Sm	ICPMS	RD
<sup>151</sup> Sm	HPLC-ICPMS	RD
<sup>152</sup> Sm	ICPMS	LR
<sup>151</sup> Eu	ICPMS	RD
<sup>153</sup> Eu	ICPMS	LR
<sup>155</sup> Eu	γ-S	ES
<sup>155</sup> Gd	ICPMS	RD
<sup>234</sup> U	ICPMS	ID
<sup>235</sup> U	ICPMS	ID
<sup>236</sup> U	ICPMS	ID
<sup>238</sup> U	ICPMS	ID, LR
<sup>237</sup> Np	ICPMS	ID
<sup>238</sup> Pu	α-S	RD, ES
<sup>239</sup> Pu	ICPMS	ID
<sup>240</sup> Pu	ICPMS	ID
<sup>241</sup> Pu	ICPMS	ID
<sup>242</sup> Pu	ICPMS	ID
<sup>241</sup> Am	γ-S	ES
<sup>242m</sup> Am	ICPMS	RD
<sup>243</sup> Am	ICPMS	ID

LR: linear regression calibration.

ID: isotope dilution analysis.

ES: external calibration of instrument response.

RD: determination of isotopic abundance on chemically separated sample with calculation of isotopic concentration by isotope ratio with nuclide that does not have isobaric interference.

All analyses were performed in duplicate or triplicate to establish the precision of the methodologies employed. Each replicate analysis was performed on aliquots from the same initial stock dissolution solution in non-consecutive analysis procedures and, in most cases, on different days. This was done so that the estimated precision took into account the procedure-to-procedure and day-to-day variability of analysis. Uranium-238, <sup>239</sup>Pu, and <sup>240</sup>Pu were determined using at least two independent calibration methods and were calculated from three replicate analyses.

The heterogeneity of these nuclides with respect to the fuel rod was assessed statistically with analysis of variance (ANOVA). This technique was used to compare the within-sample standard deviation to the between-sample standard deviation for all of nuclides determined in this work. This allows us to determine if the precision of the analytical and sampling technique is sufficient to discriminate between samples with the same nominal burnup and, therefore, identical composition.

## RESULTS AND DISCUSSION

The masses of the clad sample and the declad fuel recovered from homogenization are listed in Table 1. During the decladding process, we observed that the TMI fuel samples were physically durable, requiring three or more strikes with our modified Plattner's mortar and pestle to separate the fuel from the cladding. The cladding remained intact but could be separated from the fuel meat in one piece.

Results of analyses of the five TMI samples are given in Table 3. The precision for each nuclide was calculated from the average of the percent relative standard deviation (%RSD) for replicate analyses of the five individual dissolved TMI samples. The %RSDs varied from nuclide to nuclide but were generally <5%. Nuclides with lower concentrations, such as  $^{109}\text{Ag}$ ,  $^{149}\text{Sm}$ ,  $^{151}\text{Eu}$ , and  $^{242\text{m}}\text{Am}$ , typically had higher %RSDs. Among the Pu isotopes, the higher %RSD for the determination of  $^{238}\text{Pu}$  reflects the lower precision of  $\alpha$ -spectrometry when compared to ICPMS.

Table 3 also gives the calculated results for the fuel burnup expressed in GWd/MTU for the five samples. The propagated %RSDs for the burnups calculated for the individual TMI samples are 0.6%, 14.1%, 0.2%, 12.9%, and 1.9% for samples TMI A2, TMI B2, TMI C1, TMI C3, and TMI D2, respectively. The ICPMS method used in this work is less precise, on average, than the single-instrument precision for the traditional thermal ionization mass spectrometric method for  $^{148}\text{Nd}$  burnup determination (0.8% RSD) and slightly better on average than the  $^{137}\text{Cs}$   $\gamma$ -spectrometric method for burnup determination (5.8% RSD) [3]. The HPLC-ICPMS methodology, however, has significantly higher sample throughput, allowing replicate chemical separations and analyses to be performed in a shorter time. The poorer precisions for TMI B2 and TMI C3 are the result of these samples being the first two samples analyzed. Subsequently, several minor instrumental adjustments were implemented to improve HPLC-ICPMS precision.

Two factors need to be addressed in estimating of the total uncertainty of the fuel analysis. The first factor is the uncertainty of the analysis of the dissolved sample. The most probable uncertainty of the analysis of the dissolved fuel solutions is estimated to be  $\pm 5\%$  for nuclides with concentration  $>10^{-5}$  g/g fuel. Uranium-238 determination has an estimated most probable uncertainty of  $\pm 1\%$ . These uncertainties were estimated from analysis of quality control samples; analysis of a standard fuel, ATM-103; and experience from analyzing other samples.

Americium-242m was detected, however, at concentrations that could not be quantitated reliably in every sample. This was due to the presence of Pu in the Am-separated fraction and the need to subtract the contribution of Pu from the total signal. The lower limits were calculated as three times the standard deviation of the estimated precision of the measurement of  $m/e = 242$  in the ICPMS. Lower limits of detection will be achievable in future analyses when an HPLC procedure for actinide separation is established.

The second factor influencing the total uncertainty of the fuel analysis is analytical sampling. Spent nuclear fuel rods are heterogeneous both axially and radially. Each sample represents a discrete length from a specific fuel rod. Each sample analyzed was initially heterogeneous with respect to axial and radial distribution. The technique used in this work homogenizes the entire fuel sample with respect to the axial and radial heterogeneities. Our calculated burnup should represent a mean composition integrated over the 5-10 g of fuel. Burnup is highly dependent on the axial position of the sample. Thus, the mean burnup of the entire fuel



rod could be performed by normalization of axial gamma scans with burnups of samples determined in this work.

Table 3. Results of Analyses of Five Samples of TMI Spent Nuclear Fuel Rod Segment H6-1 by Nuclide, g/g fuel

Nuclide	TMI A2	TMI B1A	TMI C1	TMI C3	TMI D2	Precision (% RSD)
<sup>95</sup> Mo	9.88E-04	1.01E-03	9.75E-04	9.14E-04	8.29E-04	1
<sup>99</sup> Tc	9.59E-04	9.71E-04	9.52E-04	9.37E-04	8.75E-04	2
<sup>101</sup> Ru	1.03E-03	1.07E-03	1.03E-03	9.31E-04	8.50E-04	2
<sup>103</sup> Rh	5.49E-04	5.60E-04	5.46E-04	4.98E-04	4.64E-04	2
<sup>109</sup> Ag	5.3E-05	4.7E-05	4.7E-05	8.4E-05	4.2E-05	5
<sup>137</sup> Cs	1.56E-03	1.56E-03	1.60E-03	1.55E-03	1.45E-03	4
<sup>143</sup> Nd	8.46E-04	8.89E-04	8.66E-04	8.68E-04	8.22E-04	3
<sup>145</sup> Nd	7.79E-04	8.07E-04	7.93E-04	8.15E-04	7.46E-04	3
<sup>148</sup> Nd	4.88E-04	4.85E-04	4.82E-04	5.08E-04	4.39E-04	6
<sup>147</sup> Sm	1.74E-04	1.66E-04	1.65E-04	1.66E-04	1.64E-04	5
<sup>149</sup> Sm	3.38E-06	2.90E-06	2.82E-06	2.64E-06	2.79E-06	5
<sup>150</sup> Sm	3.32E-04	3.34E-04	3.39E-04	3.29E-04	3.13E-04	5
<sup>151</sup> Sm	1.11E-05	1.19E-05	1.11E-05	1.14E-05	1.14E-05	7
<sup>152</sup> Sm	1.17E-04	1.15E-04	1.12E-04	1.14E-04	1.09E-04	1
<sup>151</sup> Eu	7.8E-07	7.1E-07	6.1E-07	7.7E-07	6.3E-07	15
<sup>153</sup> Eu	1.51E-04	1.49E-04	1.48E-04	1.46E-04	1.41E-04	1
<sup>155</sup> Eu	1.14E-05	1.17E-05	1.27E-05	1.16E-05	1.11E-05	6
<sup>155</sup> Gd	4.63E-06	5.83E-06	5.62E-06	6.07E-06	5.04E-06	10
<sup>234</sup> U	1.70E-04	1.67E-04	1.75E-04	1.68E-04	1.73E-04	1
<sup>235</sup> U	5.60E-03	5.52E-03	5.82E-03	5.69E-03	6.64E-03	1
<sup>236</sup> U	4.88E-03	4.81E-03	4.83E-03	4.85E-03	4.81E-03	1
<sup>238</sup> U	8.20E-01	8.23E-01	8.17E-01	8.40E-01	8.37E-01	1
<sup>237</sup> Np	6.15E-04	6.16E-04	6.23E-04	6.21E-04	6.08E-04	1
<sup>238</sup> Pu	3.14E-04	2.80E-04	2.92E-04	2.29E-04	2.93E-04	7
<sup>239</sup> Pu	4.74E-03	4.71E-03	4.78E-03	5.01E-03	4.89E-03	3
<sup>240</sup> Pu	2.47E-03	2.43E-03	2.43E-03	2.59E-03	2.40E-03	3
<sup>241</sup> Pu	1.20E-03	1.23E-03	1.26E-03	1.28E-03	1.23E-03	3
<sup>242</sup> Pu	8.19E-04	8.14E-04	7.95E-04	8.40E-04	7.16E-04	3
<sup>241</sup> Am	2.68E-04	3.03E-04	3.33E-04	2.76E-04	3.11E-04	6
<sup>242m</sup> Am	<1E-05	<1E-05	<1E-05	<1E-05	<1E-05	-
<sup>243</sup> Am	2.25E-04	2.27E-04	2.17E-04	2.24E-04	1.74E-04	7
BU( <sup>148</sup> Nd)	50.6±0.3	50.1±7.0	50.2±0.1	51.3±6.6	44.8±0.9	

Our technique depends on the ability to produce a truly homogeneous powdered sample from which we take a random sampling. Previous work by Heinrich et al. [4] demonstrated that the method of fuel preparation used in this work does, indeed, generate a homogeneous powder. While we did not analyze multiple powdered aliquots from any single homogenized powder to reproduce the work performed in Heinrich *et al.*, we did analyze multiple samples from a single fuel rod. All five of the TMI samples were excised from four segments of a single fuel rod. The samples TMI A2, TMI B2, TMI C1, and TMI C3 essentially have the same burnup of ~51 GWd/MTU. Sample

TMI D2 has a burnup of 44.8 GWd/MTU. This burnup measurement is consistent with axial gamma scan data that indicate a 10% decrease in activity in the region of the segment where this sample originated. This sample will, therefore, be excluded from the following calculation. A comparison of the mean %RSD for duplicate analysis of each individual sample (within-sample variation) with the mean %RSD of the four nearly identical burnup samples (between-sample variation) should indicate the homogeneity of the fuel segment from which these four samples were excised, and indirectly whether each sample was homogenized. Examination of results with ANOVA (Table 4) indicated that the nuclides  $^{95}\text{Mo}$ ,  $^{101}\text{Ru}$ ,  $^{103}\text{Rh}$ ,  $^{109}\text{Ag}$ ,  $^{152}\text{Sm}$ , and  $^{235}\text{U}$  differ significantly (P value  $<0.05$ ) among the four samples. The within-sample standard deviation does not differ significantly from the between-sample standard deviation for the other 24 nuclides determined in this work. These results indicate that the section of fuel rod from which the four samples originate was homogeneous with respect to these 24 nuclides. Indirectly, these results indicate that our method produces a homogeneous powder from which we are able to sample fuel aliquots with statistically indistinguishable compositions with respect to the 24 nuclides. We conclude that our sample preparation process produced powders sufficiently homogeneous for the purpose of this work. The mean burnup of the five TMI samples is calculated to be  $49.5 \pm 2.6$  GWd/MTU. This result is consistent with the predicted value of 48.5 GWd/MTU for these segments.

## CONCLUSION

The HPLC-ICPMS demonstrates potential use as an in-line analysis method of highly irradiated PWR spent fuels in a bulk dry-powdered process. This technique was implemented without the need for separation of the plutonium, uranium, and fission products and has application for direct elemental/isotopic accountancy measurements. Development of a near-real-time method such as HPLC-ICPMS, for direct accountancy of nuclear materials is a critical step for international safeguards verification and nonproliferation policy concerns in dry-powdered processing, such as in the KAERI-DUPIC experiment and other advanced fuel cycles. Future development will eliminate the need for a separate radiochemical separation for  $^{238}\text{Pu}$  and  $^{241}\text{Pu}$  measurement. All information required for fissile accountancy of nuclear materials can then be made with one measurement.

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Table 4. Average concentrations (g/g fuel), within sample %RSD, between-sample %RSD, and ANOVA significance level for TMI A2, TMI B1A, TMI C1, and TMI C3.

Nuclide	Average Concentration	Mean within-Sample % RSD	Mean between-Sample % RSD	ANOVA P value
<sup>95</sup> Mo	9.71E-04	0.6	4.1	0.0003
<sup>99</sup> Tc	9.55E-04	1.5	1.5	0.3827
<sup>101</sup> Ru	1.01E-03	1.1	5.8	0.0012
<sup>103</sup> Rh	5.38E-04	1.6	5.1	0.0395
<sup>109</sup> Ag	5.78E-05	3.5	30.6	0.0004
<sup>137</sup> Cs	1.57E-03	2.9	1.6	0.7326
<sup>143</sup> Nd	8.67E-04	4.1	2.0	0.7665
<sup>145</sup> Nd	7.98E-04	2.3	2.0	0.7375
<sup>148</sup> Nd	4.91E-04	7.0	2.4	0.9431
<sup>147</sup> Sm	1.68E-04	6.1	2.7	0.8426
<sup>149</sup> Sm	2.93E-06	5.1	10.8	0.0574
<sup>150</sup> Sm	3.33E-04	5.9	1.3	0.9740
<sup>151</sup> Sm	1.14E-05	7.8	3.4	0.7867
<sup>152</sup> Sm	1.15E-04	0.9	1.9	0.0463
<sup>151</sup> Eu	7.17E-07	14.7	11.3	0.7205
<sup>153</sup> Eu	1.49E-04	1.1	1.6	0.1072
<sup>155</sup> Eu	1.18E-05	7.1	4.9	0.6380
<sup>155</sup> Gd	5.54E-06	10.2	11.4	0.1941
<sup>234</sup> U	1.70E-04	1.0	2.1	0.1227
<sup>235</sup> U	5.66E-03	0.6	2.3	0.0041
<sup>236</sup> U	4.84E-03	0.7	0.6	0.4595
<sup>238</sup> U	8.25E-01	1.7	1.3	0.5275
<sup>237</sup> Np	6.19E-04	1.1	0.6	0.8031
<sup>238</sup> Pu	2.79E-04	7.3	12.9	0.0589
<sup>239</sup> Pu	4.81E-03	2.9	2.9	0.5139
<sup>240</sup> Pu	2.48E-03	3.2	3.0	0.4571
<sup>241</sup> Pu	1.24E-03	3.4	2.6	0.6355
<sup>242</sup> Pu	8.17E-04	3.5	2.3	0.7011
<sup>241</sup> Am	2.95E-04	5.4	10.0	0.0708
<sup>242m</sup> Am	-	-	-	-
<sup>243</sup> Am	2.24E-04	8.9	2.1	0.9605