Journal of Radioanalytical and Nuclear Chemistry, Vol. 263, No. 3 (2005) 581–586

Analysis of high burnup spent nuclear fuel by ICP-MS

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(Received April 6, 2004)

We have used inductively coupled plasma mass spectrometry (ICP-MS) as the primary tool for determining concentrations of a suite of nuclides in samples excised from high-burnup spent nuclear fuel rods taken from light water nuclear reactors. The complete analysis included the determination of ^{95}Mo, ^{99}Tc, ^{101}Ru, ^{103}Rh, ^{109}Ag, ^{137}Cs, ^{143}Nd, ^{145}Nd, ^{148}Nd, ^{147}Sm, ^{149}Sm, ^{150}Sm, ^{151}Sm, ^{152}Sm, ^{151}Eu, ^{153}Eu, ^{155}Eu, ^{155}Gd, ^{237}Np, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu, ^{241}Am, ^{242m}Am, and ^{243}Am. The isotopic composition of fissiogenic lanthanide elements was determined using high-performance liquid chromatography (HPLC) with ICP-MS detection. These analytical results allow the determination of fuel burn-up based on ^{148}Nd, Pu, and U content, as well as provide input for storage and disposal criticality calculations. Results show that ICP-MS along with HPLC-ICP-MS are suitable of performing routine determinations of most of these nuclides, with an uncertainty of ±10% at the 95% confidence level.

Introduction

An isotopic model is being used to calculate concentrations of fissionable and neutron-absorbing nuclides for criticality evaluation of the post-closure Yucca Mountain Repository. The model used for calculating initial isotopic concentrations in commercial spent nuclear fuel is the SAS2H sequence of the Scale-4.3 computer code with the 44-energy group cross section library.[1] The validation of this isotopic model will be performed to support the License Application to the Nuclear Regulatory Commission of the proposed repository. Radiochemical assays will be used, in part, to validate the isotopic model. The fuel burnups used to validate the isotopic model to date range from 7 to 46.5 gigawatt-days per metric ton uranium (GWd/MTU). Additional radiochemical assays of higher-burnup spent nuclear fuels from both pressurized water reactors (PWR) and boiling water reactors (BWR) are required to validate the isotopic model at these burnup levels.[1]

In this study, we have used inductively coupled plasma mass spectrometry (ICP-MS) as the primary tool for determining concentrations of a suite of nuclides in 12 fuel samples with burnups >46.5 GWd/MTU, originating from the Three Mile Island (TMI-1) and Quad Cities (QC-1) reactors. The complete analysis of all samples included the determination of a suite of 31 fissionable and neutron absorbing nuclides including ^{95}Mo, ^{99}Tc, ^{101}Ru, ^{103}Rh, ^{109}Ag, ^{137}Cs, ^{143}Nd, ^{145}Nd, ^{148}Nd, ^{147}Sm, ^{149}Sm, ^{150}Sm, ^{151}Sm, ^{152}Sm, ^{151}Eu, ^{153}Eu, ^{155}Eu, ^{155}Gd, ^{237}Np, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu, ^{241}Am, ^{242m}Am, and ^{243}Am. The isotopic composition of fissiogenic lanthanide elements was determined using high-performance liquid chromatography (HPLC) with ICP-MS detection. These analytical results allow the determination of fuel burn-up based on ^{148}Nd, Pu, and U content,[2] as well as provide input for calculations potential storage and repository criticality scenarios. The primary strength of ICP-MS is the ease of sample introduction which allows rapid and routine determination of a large number of isobar-free nuclides in multiple samples. However, quadrupole-based ICP-MS systems do not possess the high precision of thermal ionization mass spectrometry (TIMS), the traditional method for the determination of Nd, U, and Pu isotopic contents of spent nuclear fuel. Consequently, it is necessary to determine the uncertainty of our analyses. We used three approaches. We analyzed a well-characterized lower-burnup fuel, ATM103 and compared our data to ORIGIN2 calculations.[3] We compared our calculated fuel burnup values with TIMS-derived values with ^{137}Cs axial scan normalization. And finally, we performed replicate determinations of samples and quality control standards in order to calculate within-sample precision, bias, and total uncertainty. As with many analytical endeavors, our goal was to devise an approach that would allow us to determine all of these 31 nuclides while maximizing throughput and accuracy for all nuclides. The accuracy goal for this project was to achieve total 95% CL uncertainties of ±10% or better for as many nuclides as possible.

Experimental

Fuel samples were cut from fuel rod segments provided by General Electric's Vallecitos Nuclear Center (GE-VNC). Five samples (TMI-1, -2, -3. -4, and -5) from TMI fuel rod H-6 were analyzed. These five samples were excised from the middle two-thirds of an approximately 15-ft UO_2 fuel rod, possessing an initial

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0236–5731/2005/USD 20.00

Akadémiai Kiadó, Budapest
Springer, Dordrecht

^{235}U enrichment of 4.0%, that was irradiated in the pressurized water reactor (PWR) TMI-1 to an estimated burnup of 48.5 GWd/MTU. Seven samples (QC-1, -2, -3, -4, -5, -6, and -7) from three fuel rods that had been irradiated in the QC-1 boiling water reactor (BWR) were analyzed. Three samples (QC-1, -2, -3) were from rod VW00101, a Zr barrier UO_2 fuel with an initial 3.0% ^{235}U enrichment and grain size of 30 mm. Two samples (QC-4 and -5) were from rod ZB00113, a Zr barrier UO_2 fuel with an initial 3.8% ^{235}U enrichment and a grain size of 15 mm, and two samples (QC-6 and -7) were from rod ZS00102, a Zr barrier UO_2–Gd_2O_3 fuel with an initial 3.0% ^{235}U enrichment, 2 wt% Gd_2O_3, and bimodal grain size. These rods are thought to have maximum burnups of 70–80 GWd/MTU for the UO_2 fuel, and a maximum burnup of ~60 GWd/MTU for the 2 wt% Gd_2O_3-UO_2 fuel.

Sample preparation

All of the sample preparation was performed at Argonne National Laboratory (ANL) in the Chemical Technology Division's (CMT) Senior Cave. The fuel was separated from the cladding using a Plattner's diamond mortar modified with a 1-m long sleeve and a 2-kg tool steel pestle, and further crushed and homogenized in hardened tool steel vials and ball pestle with a Wig-L-Bug® shaker. 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 closed-vessel dissolution method was selected in order to completely dissolve the sample, while retaining potentially volatile elements. 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 using a mixture of ultrapure Optima (Fisher Scientific) HNO_3–HCl–HF in Parr Bomb vessels equipped with Teflon® liners at 150 °C for >20 hours. The dissolved sample solution was quantitatively transferred to a weighed low-density polyethylene wash bottle by suction and the Teflon® liner was rinsed three times with 2M HNO_3. The rinse solutions were combined with the initial dissolution solution, and the wash bottle was reweighed. 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.

Sample analysis

Solution analyses were performed at ANL CMT using the ICP-MS, γ-spectrometry (γ-S), and α-spectrometry (α-S) systems previously described by WOLF.[5] Table 1 lists the nuclides analyzed, along with the analytical and calibration method used. For ICP-MS analyses, all samples from a given reactor were analyzed sequentially on the same day under routine instrumental conditions. ^{238}U was determined on a solution diluted 100-fold from the working solution by two independent calibration methods: (1) internal standardization with ^{209}Bi and external calibration via linear regression using a commercially available ^{238}U standard (SPEX Industries), and (2) isotope dilution with a ^{233}U spike (New Brunswick Laboratory, CRM 111A). The concentrations of ^{241}Am, ^{137}Cs, and ^{155}Eu were determined by direct γ-spectrometric analysis of a 5-ml aliquot of this 100-fold diluted sample. Isobar-free fission product nuclides were determined directly in the working solution by ICP-MS using internal standardization with ^{115}In and ^{209}Bi, and external calibration via linear regression using commercially available multi-element standards (SPEX Industries) with known natural abundance isotopic content. ^{99}Ru was used as a surrogate calibration element for ^{99}Tc in the standard solutions. Minor uranium isotopes, ^{237}Np, ^{239}Pu, ^{240}Pu, and ^{243}Am were determined by direct ICP-MS analysis of the working solution using the isotope dilution (ID) method with a ^{233}U isotopic spike. Other actinides were determined in chemically separated aliquots of the working solution. Actinide elements were chemically separated by anion-exchange chromatography, providing Pu fractions and Am fractions for isotope ratio (IR) determination of each element. All Pu isotopes except ^{238}Pu were determined by the ID method, with a ^{244}Pu isotopic spike (National Bureau of Standards SRM 996), including a reanalysis of ^{239}Pu and ^{240}Pu. ^{238}Pu was determined by α-spectrometry using the mean $^{239}Pu/^{240}Pu$ mass ratio that had been determined by direct analysis of the dissolved fuel with ICP-MS in the chemically separated Pu fraction. This ratio was converted to total $^{239}Pu+^{240}Pu$ activity, and the $^{239}Pu+^{240}Pu$ composite peak was used as a benchmark for the determination of ^{238}Pu by a-pulse height analysis. The isotopic composition of Am was determined from the isotopic ratio measured by ICP-MS of the chemically separated Am fraction. These ratios were corrected for the presence of small amounts of ^{242}Pu in the Am fraction, due to incomplete radiochemical separation of the two elements. The concentration of ^{242m}Am was calculated using ^{241}Am, a nuclide determined with α-spectrometry, as a benchmark.

HPLC-ICP-MS

Due to the numerous isobaric interferences, HPLC-ICP-MS was used for the purpose of determining isotopic composition of the fissiogenic lanthanide elements Nd, Sm, Eu, and Gd. A microcolumn, cationic HPLC separation based on the method described by

RÖLLIN et al.[6] was used. Separation was performed on a CG50 (2×50 mm^2) guard column coupled with a CS5A (2×250 mm^2) analytical column (Dionex Corporation), utilizing a linear gradient elution of 0.040–0.26M hydroxyisobutyric acid (HIBA) with a 0.30 ml/min flow rate. The sample injection size was 0.25 ml. The output of the analytical column was coupled directly to the ICP-MS with a CETAC MCN-100, Model M-2 pneumatic microconcentric nebulizer (CETAC Technologies). A chromatogram for a 0.25 ml sample of QC-3 is shown in Fig. 1. The relative isotopic abundance of individual isotopes of each element was measured by ICP-MS. ICP-MS time resolved analysis (TRA) was performed by scanning from 140–160 amu with a 320 μs and 20-channel/amu dwell time. The absolute concentration of each isotope could then be calculated relative to the absolute concentration of an isobar-free nuclide, as determined from direct ICP-MS analysis. ^{152}Sm, ^{153}Eu, and ^{156}Gd were used as benchmark nuclides for their respective elements. Nd isotopes were determined by ID with a ^{150}Nd isotopic spike (provided in-house by ANL Analytical Chemistry Laboratory) for definitive results.

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. ^{238}U, ^{239}Pu, and ^{240}Pu concentrations were determined using at least two independent calibration methods, and were calculated from three replicate analyses. Additionally, all analyzed samples were bracketed with quality control (QC) samples so that bias uncertainty could be estimated.

Results and discussion

Results of our analyses of ATM103 and concentrations predicted by ORIGEN2 calculations[2] are given in Table 1. Table 1 also shows our calculated fuel burnup and fuel burnup for a sample of the same fuel with similar axial location reported previously.[3] The ORIGEN2 values have been linearly extrapolated to correct for burnup and decay time. Comparisons show that most nuclides were within ±10% of ORIGEN2 values with a trend of slightly larger errors for lower concentration nuclides. ^{109}Ag shows a significant deviation of –63%, potentially due to the uncertainty of the behavior of Ag in the irradiated fuel. Slightly higher relative errors are observed in nuclides that possess significant potential isobaric interferences and thus, required either chemical separations with direct ID determination (^{241}Pu, and ^{242}Pu) or chemical separation followed by IR determination with benchmarking to a separately determined nuclide (^{147}Sm, ^{150}Sm, ^{151}Eu, ^{155}Gd, ^{238}Pu, and ^{242m}Am).

Results of nuclide analyses and calculated fuel burnup for the five TMI and 7 QC samples are given in Table 2. Fuel burnups were calculated according to ASTM E 321-79.[2] The mean burnup of the five analyzed TMI samples is calculated to be 49.5±2.6 GWd/MTU, consistent with the predicted value of 48.5 GWd/MTU for these segments. These burnup values, along with those calculated from ^{137}Cs scans, are listed in Table 3 for comparison purposes. Six of the seven samples are within ±4% of the ^{148}Nd-normalized gamma scan value with five of these results within ±2.5%. Our value for sample QC-6 is –8.4% relative to the ^{148}Nd-normalized gamma scan value.

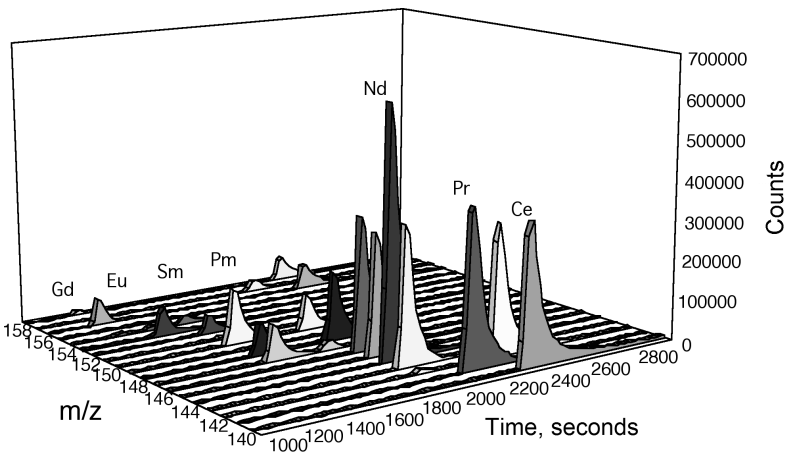

Fig. 1. HPLC-ICPMS chromatogram for a 0.25-ml sample of dissolved high-burnup fuel sample QC-3.
Chemical separation achieved by this method allows for complete isotopic determination of the fissiogenic lanthanide elements

Table 1. Analytical techniques, calibration methods, results of analyses of ATM103, ORIGEN2 calculations, and comparison of analyses with calculated concentrations for nuclides determined in this work

Nuclide	Technique	Calibration method	This work	ORIGEN2[1]	Relative error, %
^{95}Mo	ICP-MS	LR	$6.80\cdot10^{-4}$	$6.50\cdot10^{-4}$	4.5
^{99}Tc	ICP-MS	LR	$6.62\cdot10^{-4}$	$6.73\cdot10^{-4}$	–1.6
^{101}Ru	ICP-MS	LR	$6.93\cdot10^{-4}$	$6.86\cdot10^{-4}$	0.9
^{103}Rh	ICP-MS	LR	$3.98\cdot10^{-4}$	$4.10\cdot10^{-4}$	–3.0
^{109}Ag	ICP-MS	LR	$2.81\cdot10^{-5}$	$7.56\cdot10^{-5}$	–63
^{137}Cs	γ-S	ES	$6.48\cdot10^{-4}$	$6.43\cdot10^{-4}$	0.8
^{143}Nd	ICP-MS	LR, ID	$6.14\cdot10^{-4}$	$6.49\cdot10^{-4}$	–5.4
^{145}Nd	ICP-MS	LR, ID	$5.58\cdot10^{-4}$	$5.78\cdot10^{-4}$	–3.6
^{148}Nd	HPLC-ICP-MS	ID	$3.22\cdot10^{-4}$	$3.26\cdot10^{-4}$	–1.3
^{147}Sm	HPLC-ICP-MS	RD	$2.12\cdot10^{-4}$	$1.75\cdot10^{-4}$	21
^{149}Sm	ICP-MS	LR, ID	$2.16\cdot10^{-6}$	$2.05\cdot10^{-6}$	5.4
^{150}Sm	ICP-MS	RD	$2.35\cdot10^{-4}$	$2.16\cdot10^{-4}$	8.6
^{151}Sm	HPLC-ICP-MS	RD	$8.20\cdot10^{-6}$	$9.02\cdot10^{-6}$	–9.1
^{152}Sm	ICP-MS	LR	$1.05\cdot10^{-4}$	$1.12\cdot10^{-4}$	–6.4
^{151}Eu	ICP-MS	RD	$1.33\cdot10^{-6}$	$1.59\cdot10^{-6}$	–16
^{153}Eu	ICP-MS	LR	$1.05\cdot10^{-4}$	$9.81\cdot10^{-5}$	7.0
^{155}Eu	γ-S	ES	$6.37\cdot10^{-7}$	$6.69\cdot10^{-7}$	–4.8
^{155}Gd	ICP-MS	RD	$9.53\cdot10^{-6}$	$1.26\cdot10^{-5}$	–24
^{234}U	ICP-MS	ID	$1.45\cdot10^{-4}$	$1.38\cdot10^{-4}$	5.3
^{235}U	ICP-MS	ID	$4.79\cdot10^{-3}$	$5.15\cdot10^{-3}$	–7.0
^{236}U	ICP-MS	ID	$3.04\cdot10^{-3}$	$3.06\cdot10^{-3}$	–0.42
^{238}U	ICP-MS	ID, LR	$8.47\cdot10^{-1}$	$8.34\cdot10^{-1}$	1.6
^{237}Np	ICP-MS	ID	$3.43\cdot10^{-4}$	$4.00\cdot10^{-4}$	–14
^{238}Pu	α-S	RD, ES	$1.50\cdot10^{-4}$	$1.31\cdot10^{-4}$	15
^{239}Pu	ICP-MS	ID	$4.50\cdot10^{-3}$	$4.47\cdot10^{-3}$	0.7
^{240}Pu	ICP-MS	ID	$2.18\cdot10^{-3}$	$2.15\cdot10^{-3}$	1.4
^{241}Pu	ICP-MS	ID	$4.80\cdot10^{-4}$	$4.22\cdot10^{-4}$	14
^{242}Pu	ICP-MS	ID	$4.47\cdot10^{-4}$	$4.93\cdot10^{-4}$	–9.2
^{241}Am	γ-S	ES	$7.58\cdot10^{-4}$	$7.68\cdot10^{-4}$	–1.3
^{242m}Am	ICP-MS	RD	$1.00\cdot10^{-6}$	$8.88\cdot10^{-7}$	13
^{243}Am	ICP-MS	ID	$1.00\cdot10^{-4}$	$1.05\cdot10^{-4}$	–4.7
Burnup:			33.2	33.17	0.09

LR: Linear regression calibration.
ID: Isotope dilution analysis.
ES: External calibration of instrument response.
RD: Isotope ratio calculation benchmarked to isobar-free isotope.

The average precision of our burnup analyses are 4.2% RSD, slightly higher to the single instrument ^{148}Nd/U TIMS precision (0.9%) but lower than the single instrument ^{137}Cs/U method (5.8%).[7]

The within-sample precision, bias uncertainty, and total uncertainty at the 95% confidence limits are given in Table 4. All values are expressed in terms of percent, relative to the concentration of the nuclide in the fuel. Both the estimated within-sample precision and the bias uncertainty values reflect the uncertainties in the analytical measurement and calibration techniques employed in this work. The bias uncertainty of analysis was calculated as the root sum of square deviation from expected QC solution concentrations that were analyzed before and after the fuel samples. Total 95% CL uncertainties were calculated according to ASTM E691-79.[8] Relative uncertainties are nuclide dependent, and range from 3.7 to 23%, with an average uncertainty of 8.3%.

Table 2. Results of analyses of 12 samples of TMI and QC spent nuclear fuel rod segment nuclide (in g/g fuel)

Nuclide	TMI–1	TMI–2	TMI–3	TMI–4	TMI–5	QC–1	QC–2	QC–3	QC–4	QC–5	QC–6	QC–7
^{95}Mo	$9.88\cdot10^{-4}$	$1.01\cdot10^{-3}$	$9.75\cdot10^{-4}$	$9.14\cdot10^{-4}$	$8.29\cdot10^{-4}$	$9.97\cdot10^{-4}$	$1.06\cdot10^{-3}$	$9.83\cdot10^{-4}$	$1.03\cdot10^{-3}$	$9.01\cdot10^{-4}$	$1.17\cdot10^{-3}$	$9.50\cdot10^{-4}$
^{99}Tc	$9.59\cdot10^{-4}$	$9.71\cdot10^{-4}$	$9.52\cdot10^{-4}$	$9.37\cdot10^{-4}$	$8.75\cdot10^{-4}$	$1.14\cdot10^{-3}$	$1.15\cdot10^{-3}$	$1.14\cdot10^{-3}$	$1.10\cdot10^{-3}$	$1.04\cdot10^{-3}$	$1.23\cdot10^{-3}$	$1.10\cdot10^{-3}$
^{101}Ru	$1.03\cdot10^{-3}$	$1.07\cdot10^{-3}$	$1.03\cdot10^{-3}$	$9.31\cdot10^{-4}$	$8.50\cdot10^{-4}$	$1.16\cdot10^{-3}$	$1.25\cdot10^{-3}$	$1.15\cdot10^{-3}$	$1.15\cdot10^{-3}$	$1.03\cdot10^{-3}$	$1.30\cdot10^{-3}$	$1.04\cdot10^{-3}$
^{103}Rh	$5.49\cdot10^{-4}$	$5.60\cdot10^{-4}$	$5.46\cdot10^{-4}$	$4.98\cdot10^{-4}$	$4.64\cdot10^{-4}$	$4.65\cdot10^{-4}$	$5.16\cdot10^{-4}$	$4.90\cdot10^{-4}$	$5.30\cdot10^{-4}$	$4.75\cdot10^{-4}$	$5.65\cdot10^{-4}$	$5.08\cdot10^{-4}$
^{109}Ag	$5.3\cdot10^{-5}$	$4.7\cdot10^{-5}$	$4.7\cdot10^{-5}$	$8.4\cdot10^{-5}$	$4.2\cdot10^{-5}$	$3.52\cdot10^{-5}$	$7.69\cdot10^{-5}$	$6.29\cdot10^{-5}$	$4.60\cdot10^{-5}$	$6.12\cdot10^{-5}$	$1.04\cdot10^{-4}$	$3.93\cdot10^{-5}$
^{137}Cs	$1.56\cdot10^{-3}$	$1.56\cdot10^{-3}$	$1.60\cdot10^{-3}$	$1.55\cdot10^{-3}$	$1.45\cdot10^{-3}$	$1.81\cdot10^{-3}$	$1.54\cdot10^{-3}$	$1.87\cdot10^{-3}$	$1.42\cdot10^{-3}$	$1.57\cdot10^{-3}$	$1.61\cdot10^{-3}$	$1.65\cdot10^{-3}$
^{143}Nd	$8.46\cdot10^{-4}$	$8.89\cdot10^{-4}$	$8.66\cdot10^{-4}$	$8.68\cdot10^{-4}$	$8.22\cdot10^{-4}$	$4.83\cdot10^{-4}$	$5.45\cdot10^{-4}$	$5.71\cdot10^{-4}$	$6.70\cdot10^{-4}$	$7.07\cdot10^{-4}$	$6.78\cdot10^{-4}$	$8.19\cdot10^{-4}$
^{145}Nd	$7.79\cdot10^{-4}$	$8.07\cdot10^{-4}$	$7.93\cdot10^{-4}$	$8.15\cdot10^{-4}$	$7.46\cdot10^{-4}$	$8.90\cdot10^{-4}$	$9.17\cdot10^{-4}$	$8.69\cdot10^{-4}$	$8.70\cdot10^{-4}$	$8.15\cdot10^{-4}$	$9.36\cdot10^{-4}$	$8.86\cdot10^{-4}$
^{148}Nd	$4.88\cdot10^{-4}$	$4.85\cdot10^{-4}$	$4.82\cdot10^{-4}$	$5.08\cdot10^{-4}$	$4.39\cdot10^{-4}$	$6.31\cdot10^{-4}$	$6.45\cdot10^{-4}$	$6.25\cdot10^{-4}$	$5.91\cdot10^{-4}$	$5.33\cdot10^{-4}$	$6.41\cdot10^{-4}$	$5.53\cdot10^{-4}$
^{147}Sm	$1.74\cdot10^{-4}$	$1.66\cdot10^{-4}$	$1.65\cdot10^{-4}$	$1.66\cdot10^{-4}$	$1.64\cdot10^{-4}$	$2.37\cdot10^{-4}$	$2.44\cdot10^{-4}$	$2.24\cdot10^{-4}$	$2.42\cdot10^{-4}$	$2.22\cdot10^{-4}$	$2.75\cdot10^{-4}$	$2.57\cdot10^{-4}$
^{149}Sm	$3.38\cdot10^{-6}$	$2.90\cdot10^{-6}$	$2.82\cdot10^{-6}$	$2.64\cdot10^{-6}$	$2.79\cdot10^{-6}$	$1.00\cdot10^{-6}$	$1.21\cdot10^{-6}$	$1.41\cdot10^{-6}$	$1.39\cdot10^{-6}$	$1.79\cdot10^{-6}$	$1.12\cdot10^{-6}$	$1.70\cdot10^{-6}$
^{150}Sm	$3.32\cdot10^{-4}$	$3.34\cdot10^{-4}$	$3.39\cdot10^{-4}$	$3.29\cdot10^{-4}$	$3.13\cdot10^{-4}$	$3.20\cdot10^{-4}$	$3.59\cdot10^{-4}$	$3.13\cdot10^{-4}$	$3.40\cdot10^{-4}$	$3.01\cdot10^{-4}$	$3.99\cdot10^{-4}$	$3.07\cdot10^{-4}$
^{151}Sm	$1.11\cdot10^{-5}$	$1.19\cdot10^{-5}$	$1.11\cdot10^{-5}$	$1.14\cdot10^{-5}$	$1.14\cdot10^{-5}$	$6.07\cdot10^{-6}$	$6.73\cdot10^{-6}$	$6.36\cdot10^{-6}$	$8.91\cdot10^{-6}$	$8.95\cdot10^{-6}$	$8.07\cdot10^{-6}$	$7.87\cdot10^{-6}$
^{152}Sm	$1.17\cdot10^{-4}$	$1.15\cdot10^{-4}$	$1.12\cdot10^{-4}$	$1.14\cdot10^{-4}$	$1.09\cdot10^{-4}$	$1.37\cdot10^{-4}$	$1.47\cdot10^{-4}$	$1.28\cdot10^{-4}$	$1.23\cdot10^{-4}$	$1.05\cdot10^{-4}$	$1.48\cdot10^{-4}$	$1.20\cdot10^{-4}$
^{151}Eu	$7.8\cdot10^{-7}$	$7.1\cdot10^{-7}$	$6.1\cdot10^{-7}$	$7.7\cdot10^{-7}$	$6.3\cdot10^{-7}$	$5.82\cdot10^{-7}$	$5.60\cdot10^{-7}$	$6.55\cdot10^{-7}$	$7.86\cdot10^{-7}$	$8.78\cdot10^{-7}$	$6.29\cdot10^{-7}$	$8.65\cdot10^{-7}$
^{153}Eu	$1.51\cdot10^{-4}$	$1.49\cdot10^{-4}$	$1.48\cdot10^{-4}$	$1.46\cdot10^{-4}$	$1.41\cdot10^{-4}$	$1.61\cdot10^{-4}$	$1.77\cdot10^{-4}$	$1.62\cdot10^{-4}$	$1.75\cdot10^{-4}$	$1.97\cdot10^{-4}$	$1.85\cdot10^{-4}$	$1.53\cdot10^{-4}$
^{155}Eu	$1.14\cdot10^{-5}$	$1.17\cdot10^{-5}$	$1.27\cdot10^{-5}$	$1.16\cdot10^{-5}$	$1.11\cdot10^{-5}$	$7.96\cdot10^{-6}$	$7.66\cdot10^{-6}$	$8.49\cdot10^{-6}$	$8.31\cdot10^{-6}$	$8.19\cdot10^{-6}$	$6.51\cdot10^{-6}$	$7.07\cdot10^{-6}$
^{155}Gd	$4.63\cdot10^{-6}$	$5.83\cdot10^{-6}$	$5.62\cdot10^{-6}$	$6.07\cdot10^{-6}$	$5.04\cdot10^{-6}$	$9.32\cdot10^{-6}$	$1.06\cdot10^{-5}$	$1.20\cdot10^{-5}$	$1.04\cdot10^{-5}$	$1.13\cdot10^{-5}$	$1.21\cdot10^{-5}$	$1.05\cdot10^{-5}$
^{234}U	$1.70\cdot10^{-4}$	$1.67\cdot10^{-4}$	$1.75\cdot10^{-4}$	$1.68\cdot10^{-4}$	$1.73\cdot10^{-4}$	$8.39\cdot10^{-5}$	$8.30\cdot10^{-5}$	$9.15\cdot10^{-5}$	$1.11\cdot10^{-4}$	$1.15\cdot10^{-4}$	$1.18\cdot10^{-4}$	$1.39\cdot10^{-4}$
^{235}U	$5.60\cdot10^{-3}$	$5.52\cdot10^{-3}$	$5.82\cdot10^{-3}$	$5.69\cdot10^{-3}$	$6.64\cdot10^{-3}$	$2.25\cdot10^{-4}$	$2.61\cdot10^{-4}$	$4.38\cdot10^{-4}$	$7.72\cdot10^{-4}$	$1.17\cdot10^{-3}$	$9.05\cdot10^{-4}$	$2.49\cdot10^{-3}$
^{236}U	$4.88\cdot10^{-3}$	$4.81\cdot10^{-3}$	$4.83\cdot10^{-3}$	$4.85\cdot10^{-3}$	$4.81\cdot10^{-3}$	$3.47\cdot10^{-3}$	$3.34\cdot10^{-3}$	$3.51\cdot10^{-3}$	$2.98\cdot10^{-3}$	$3.54\cdot10^{-3}$	$3.43\cdot10^{-3}$	$4.57\cdot10^{-3}$
^{238}U	$8.20\cdot10^{-1}$	$8.23\cdot10^{-1}$	$8.17\cdot10^{-1}$	$8.40\cdot10^{-1}$	$8.37\cdot10^{-1}$	$7.53\cdot10^{-1}$	$7.54\cdot10^{-1}$	$7.68\cdot10^{-1}$	$7.72\cdot10^{-1}$	$7.56\cdot10^{-1}$	$7.55\cdot10^{-1}$	$7.51\cdot10^{-1}$
^{237}Np	$6.15\cdot10^{-4}$	$6.16\cdot10^{-4}$	$6.23\cdot10^{-4}$	$6.21\cdot10^{-4}$	$6.08\cdot10^{-4}$	$4.50\cdot10^{-4}$	$4.86\cdot10^{-4}$	$5.06\cdot10^{-4}$	$5.53\cdot10^{-4}$	$5.45\cdot10^{-4}$	$6.28\cdot10^{-4}$	$5.05\cdot10^{-4}$
^{238}Pu	$3.14\cdot10^{-4}$	$2.80\cdot10^{-4}$	$2.92\cdot10^{-4}$	$2.29\cdot10^{-4}$	$2.93\cdot10^{-4}$	$3.25\cdot10^{-4}$	$4.35\cdot10^{-4}$	$3.62\cdot10^{-4}$	$4.07\cdot10^{-4}$	$3.99\cdot10^{-4}$	$4.61\cdot10^{-4}$	$4.16\cdot10^{-4}$
^{239}Pu	$4.74\cdot10^{-3}$	$4.71\cdot10^{-3}$	$4.78\cdot10^{-3}$	$5.01\cdot10^{-3}$	$4.89\cdot10^{-3}$	$2.40\cdot10^{-3}$	$2.83\cdot10^{-3}$	$2.90\cdot10^{-3}$	$4.37\cdot10^{-3}$	$4.33\cdot10^{-3}$	$3.03\cdot10^{-3}$	$3.55\cdot10^{-3}$
^{240}Pu	$2.47\cdot10^{-3}$	$2.43\cdot10^{-3}$	$2.43\cdot10^{-3}$	$2.59\cdot10^{-3}$	$2.40\cdot10^{-3}$	$2.37\cdot10^{-3}$	$2.71\cdot10^{-3}$	$2.56\cdot10^{-3}$	$2.79\cdot10^{-3}$	$2.51\cdot10^{-3}$	$2.60\cdot10^{-3}$	$2.54\cdot10^{-3}$
^{241}Pu	$1.20\cdot10^{-3}$	$1.23\cdot10^{-3}$	$1.26\cdot10^{-3}$	$1.28\cdot10^{-3}$	$1.23\cdot10^{-3}$	$5.52\cdot10^{-4}$	$7.41\cdot10^{-4}$	$6.69\cdot10^{-4}$	$1.02\cdot10^{-3}$	$8.82\cdot10^{-4}$	$7.66\cdot10^{-4}$	$8.18\cdot10^{-4}$
^{242}Pu	$8.19\cdot10^{-4}$	$8.14\cdot10^{-4}$	$7.95\cdot10^{-4}$	$8.40\cdot10^{-4}$	$7.16\cdot10^{-4}$	$1.63\cdot10^{-3}$	$1.77\cdot10^{-3}$	$1.57\cdot10^{-3}$	$1.42\cdot10^{-3}$	$1.15\cdot10^{-3}$	$1.37\cdot10^{-3}$	$1.08\cdot10^{-3}$
^{241}Am	$2.68\cdot10^{-4}$	$3.03\cdot10^{-4}$	$3.33\cdot10^{-4}$	$2.76\cdot10^{-4}$	$3.11\cdot10^{-4}$	$3.35\cdot10^{-4}$	$2.84\cdot10^{-4}$	$4.05\cdot10^{-4}$	$4.54\cdot10^{-4}$	$5.92\cdot10^{-4}$	$4.86\cdot10^{-4}$	$4.73\cdot10^{-4}$
^{242m}Am	$<1\cdot10^{-5}$	$<1\cdot10^{-5}$	$<1\cdot10^{-5}$	$<1\cdot10^{-5}$	$<1\cdot10^{-5}$	$<1\cdot10^{-5}$	$<1\cdot10^{-5}$	$<1\cdot10^{-5}$	$2.41\cdot10^{-7}$	$<1\cdot10^{-5}$	$2.08\cdot10^{-6}$	$<1\cdot10^{-5}$
^{243}Am	$2.25\cdot10^{-4}$	$2.27\cdot10^{-4}$	$2.17\cdot10^{-4}$	$2.24\cdot10^{-4}$	$1.74\cdot10^{-4}$	$5.01\cdot10^{-4}$	$4.51\cdot10^{-4}$	$4.73\cdot10^{-4}$	$4.11\cdot10^{-4}$	$4.32\cdot10^{-4}$	$5.61\cdot10^{-4}$	$3.14\cdot10^{-4}$

Table 3. Calculated burnup and 1σ precision for 12 spent nuclear fuel samples analyzed in this work. Burnups are calculated based on atom percent ^{148}Nd fission.[7] Results are compared to with TIMS derived values with ^{137}Cs axial scan normalization

Sample	Burnup, this work, GWd/MTU	Burnup,* GE-VNC, GWd/MTU
TMI-1	50.6 ± 0.3	–
TMI-2	50.1 ± 7.0	–
TMI-3	50.2 ± 0.1	–
TMI-4	51.3 ± 6.6	–
TMI-5	44.8 ± 0.9	–
TMI mean:	49.4 ± 2.6	48.5
QC-1	70.4 ± 1.1	71.2
QC-2	71.7 ± 2.1	72.6
QC-3	68.4 ± 3.7	69.6
QC-4	64.4 ± 2.6	62.0
QC-5	59.7 ± 1.7	61.1
QC-6	71.1 ± 0.5	77.6
QC-7	62.0 ± 2.1	63.6

* ^{137}Cs scan normalized to ^{148}Nd.

Table 4. Estimates for method within-sample standard deviation, root sum of square deviation from mean, and total uncertainty for each nuclide

Nuclide	Within-sample precision, % rsd	Bias uncertainty, rel. %	Total uncertainty, 95% CL
^{95}Mo	1.7	2.2	4.9
^{99}Tc	2.7	1.5	5
^{101}Ru	1.6	4.5	9
^{103}Rh	1.5	1.5	3.7
^{109}Ag	4.7	1.7	9.2
^{137}Cs	3.6	0.5	7.1
^{143}Nd	3.5	2.9	7.4
^{145}Nd	4.8	2.4	9.4
^{148}Nd	4.2	2.2	8
^{147}Sm	3.3	9.0	18
^{149}Sm	7.1	2.3	14
^{150}Sm	3.5	1.8	6.8
^{151}Sm	6.1	1.8	12
^{152}Sm	2.7	1.8	5.4
^{151}Eu	12	1.2	23
^{153}Eu	3.9	1.4	7.5
^{155}Eu	6.4	0.5	12
^{155}Gd	6.8	2.7	13
^{234}U	3.0	0.5	5.9
^{235}U	1.5	1.1	2.9
^{236}U	4.6	1.6	9.0
^{238}U	1.7	2.7	5.7
^{237}Np	4.1	2.1	8.0
^{238}Pu	6.8	2.4	13
^{239}Pu	4.3	1.9	8.5
^{240}Pu	5.1	1.5	10
^{241}Pu	3.2	1.1	6.2
^{242}Pu	5.9	0.7	12
^{241}Am	6.1	1.5	12
^{242m}Am	5.1	1.6	10
^{243}Am	4.2	2.7	8.3

Conclusions

Our results show that ICP-MS along with the hybrid technique HPLC-ICPMS is capable of performing routine determinations of a large suite of fissionable and neutron-absorbing nuclides in high burnup spent nuclear fuel. The total 95% CL uncertainties are nuclide dependent and range from 3.7 to 23% with an average of 8.3%. The average precision of our burnup analyses are 4.2% RSD, which lies between the precisions typically obtained by TIMS (0.9%) and the single instrument ^{137}Cs/U method (5.8%).[7] Considering the complete scope of nuclides determined, our analytical methodology these results compare favorably to these two methods and should be considered as a viable alternative for spent nuclear fuel analysis.

*

This work was supported by the Yucca Mountain Project. The author would like to thank Mark CLARK, John FALKENBERG, and Jeff EMERY for their assistance.

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