

# Determination of Light Water Reactor Fuel Burnup with the Isotope Ratio Method

David C. Gerlach  
Mark R. Mitchell  
Bruce D. Reid

Christopher J. Gesh  
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October 2007

Work performed for the  
Office of Defense Nuclear Nonproliferation (NA-20)  
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Richland, Washington 99352

## Summary

The overall goal of this project is to develop a means of measuring light water reactor (LWR) fuel assembly burnup independent of time passed since the assembly was discharged from the reactor. Assembly burnup could be used to objectively verify that reactor operation was in accordance with declared operations, for example targets intended to produce weapons-usable material were not irradiated. The specific goal of the research covered by this report is to evaluate whether the isotope ratio method can produce meaningful results that can be used to infer fuel burnup in light water power reactors. We present new measurements that were completed on irradiated and unirradiated zirconium alloys and the results of preliminary reactor calculations. Zirconium alloys are used for structural elements of fuel assemblies and for the fuel element cladding. Unirradiated zircaloy samples served as reference samples and indicate starting or natural values for the Ti isotope ratio measured. We measured four irradiated samples provided by a fuel vendor. New results indicate:

1. Titanium isotope ratios, particularly  $^{49}\text{Ti}/^{48}\text{Ti}$  ratios, in unirradiated zircaloy samples were indistinguishably close to values determined several months earlier and very close to expected natural values. The small difference from natural values represents measurement bias typical of mass spectrometric analytical methods. This has implications for improving accuracy and precision in measurements by simply using results obtained on unirradiated samples as starting values and removing the contributing factor of instrument mass bias corrections.
2. Furthermore, there is little or no variation in Ti ratios between the various samples, indicating that zircaloys likely have experienced no relative fractionation or changes of Ti ratios during refinement and production
3. Titanium isotope ratios measured in four irradiated samples demonstrated marked departures from natural or initial ratios, well beyond analytical uncertainty, and showed that ratios vary in a self-consistent manner with reported fluence values.
4. Other activated impurity elements still limit the sample size for secondary ionization mass spectrometry (SIMS) analysis of irradiated samples. The sample fragments used for SIMS analysis, although smaller than optimal, were still analyzed successfully without violating the radiological limits of the instrument location, and this effectively reduces the cost of sample handling and analyses.

Additionally, preliminary reactor calculations have been performed to estimate the energy production of the fuel adjacent to the sample locations. The resulting burnup estimates are reasonable, but must be regarded as preliminary since the calculations are based on incomplete fuel design information. We intend to follow up the preliminary reactor physics calculations with best estimate calculations once we get the appropriate fuel cycle information on the fuel assemblies from which the samples were acquired.



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## 1.0 Introduction

This report describes progress in studying the feasibility of using stable isotopic ratios of titanium as signatures of reactor operating history and conditions. This technique can provide objective evidence that the operation of an LWR reactor was or was not in accordance with declared conditions. Secondary Ionization Mass Spectrometry (SIMS) was used to measure titanium isotope ratios in four newly obtained samples of irradiated zirconium alloys obtained from a fuel vendor. For purposes of retaining background information and previous results for comparison, much of the information from the previous technical report is provided in Appendix B of this report.

The isotope ratio method (IRM) is a technique for estimating the energy production in a fission reactor by measuring isotope ratios in non-fuel reactor components. The isotope ratios in these components can then be directly related to the cumulative energy production with standard reactor calculations.

All reactor materials contain trace elemental impurities at parts-per-million levels, and the isotopes of these elements are transmuted by neutron irradiation in a predictable manner. While measuring the change in a particular isotope's concentration is possible, it is difficult to correlate to energy production because the initial concentration of that element may not be known. However, if the ratio of two isotopes of the same element can be measured, the energy production can then be determined without knowing the absolute concentration of that impurity since the initial natural ratio is known. This is the fundamental principle underlying the IRM. Extremely sensitive mass-spectrometric methods are currently available that allow accurate measurements of the impurity isotope ratios in a sample. Additionally, indicator elements with stable activation products have been identified so that their post-irradiation isotope ratios remain constant.

IRM has been successfully demonstrated on graphite-moderated reactors. Graphite reactors are particularly well-suited to such analyses since the graphite moderator is resident in the active core for the entire period of operation. Applying this method to other reactor types is more difficult since the resident portions of the reactor structure available for sampling are typically outside the active core. This research evaluated whether the IRM can produce meaningful results for light water power reactors by examining zircaloy samples from the reactor core.

## 2.0 Proof-of-Principle Analyses of Irradiated Zircaloy Samples

### 2.1 Sample preparations and SIMS analysis approaches and observations

Sub-samples consisting of thin wafers, 3 mm in diameter, designed for later transmission electron microscope studies, were supplied to PNNL by a fuel vendor. These samples were cut from the zirconium channel that surrounds Boiling Water Reactor (BWR) fuel assemblies during irradiation. Six wafers from each of eight sampled reactor positions were provided. Dose rate and gamma analyses for each of the eight sample batches were also provided (Appendix A, Table 3). The gamma counting data also provided guidance in how much of a single wafer was needed, or could be allowed, for SIMS analysis.

To date, SIMS analysis has been performed on only four of the eight sample batches. A single wafer was selected from each of these four sample batches and prepared for SIMS analysis. For titanium isotope ratios, masses  $^{46}\text{Ti}$ ,  $^{47}\text{Ti}$ ,  $^{48}\text{Ti}$ , and  $^{49}\text{Ti}$  were analyzed. Ions with a mass of 50 were excluded because of possible Cr and V isobaric interferences. Since  $^{50}\text{Ti}$  is less sensitive to burnup determinations it can be excluded from analysis without loss of accuracy. Doubly-charged ions typically are detected as having half their atomic mass in the SIMS or other mass spectrometers. Since zirconium has atomic masses about twice that of most of the titanium masses, doubly-charged zirconium ions create significant interferences added to the titanium ion signals of interest. While even-mass-numbered, doubly-charged zirconium ions cannot be distinguished from singly-charged Ti ions of half their atomic mass, a double charged ion arising from an odd mass such as  $^{91}\text{Zr}$  is useful for making corrections on the Ti isotope ion counts. A half-mass position was monitored at mass 45.455 to determine corrections necessary for  $\text{Zr}^{+2}$  interferences in the Ti mass range. Up to 80% or more of the counts at mass 48 are due to  $\text{Zr}^{+2}$ . Despite the magnitude of this interference correction, ion signals from the impurity Ti and the matrix  $\text{Zr}^{+2}$  tend to be stable and constant, and as a results, measured Ti isotope ratios are reproducible to about 1%. In contrast, lower amounts (20-40%) of the ion counts at mass 48 were due to this interference in the irradiated samples analyzed and described below.

Prior to starting analyses of the radioactive samples from the fuel vendor, new analyses of Ti isotope ratios were performed on several of the unirradiated samples of zirconium alloys obtained previously, especially Zr-2 and Zr-4 types, to confirm SIMS instrument settings for analysis, and to determine initial or natural values of Ti isotope ratios. Since Ti isotope ratios vary little in natural geologic or cosmic samples, values determined on these starting materials can be used as initial values in later modeling calculations and the contribution of uncertainty to sample measurement precision and accuracy due to instrument measurement mass bias can be excluded. Based on measurement of these representative starting materials, only  $^{49}\text{Ti}/^{48}\text{Ti}$  is constant and useful.

### 2.2 Preliminary SIMS Results on Irradiated Samples

Initial  $^{49}\text{Ti}/^{48}\text{Ti}$  ratios measured in fuel vendor irradiated samples were unexpectedly close to natural values, due to  $^{48}\text{Ca}$  and  $^{24}\text{Mg}^{2+}$  ions contributing to ion counts at mass 48. In order to track the contributions from these impurities,  $^{44}\text{Ca}$  and  $^{24}\text{Mg}$  ions were monitored along with the aforementioned titanium and 45.455 mass ions. Resulting  $^{49}\text{Ti}/^{48}\text{Ti}$  ratios are reported for analyses where the  $^{44}\text{Ca}/48$  and  $^{24}\text{Mg}/48$  ratios were low enough that contributions from these interferences were low or negligible. These impurities were not observed in the nonradioactive reference samples, but were present to varying degrees

in the fuel vendor samples. The Ca and Mg ion signals usually decreased significantly to near-negligible levels after 30 minutes or more of presputtering and the removal of surface contamination with the SIMS primary ion beam (Appendix A, Figure A.1), although occasionally, increases were observed at some depth in samples, which appear to indicate impurity inclusions with elevated contents of these elements (Appendix A, Figure A.2). Small inclusions higher in Ti, relative to the baseline or matrix impurity levels, were also observed at times. Best results are obtained when the Ca and Mg contributions were low and all ion signals stable, as exemplified in Figure A.3 (Appendix A). It is possible that some surficial Ca and Mg were added during sample handling and mounting. It may also be possible that the fuel vendor Zr alloy samples were either not as pure or homogeneous as the vendor-supplied Zr-2 and Zr-4 samples, or that impurities were added during exposure in the reactor or during extraction from the reactor.

Compared with  $^{49}\text{Ti}/^{48}\text{Ti}$  ratios determined in the unirradiated Zr-2 and Zr-4 vendor-supplied samples,  $^{49}\text{Ti}/^{48}\text{Ti}$  ratios determined thus far in four different irradiated fuel vendor samples are (after corrections for the above-discussed interferences) substantially higher than natural or initial Ti ratios as expected (Table 1) and clearly indicate changes with neutron fluence exposure and fuel burnup.

**Table 1.** SIMS measurements of  $^{49}\text{Ti}/^{48}\text{Ti}$  ratios in four reference samples (first four entries) and four irradiated zircaloy samples supplied by a fuel vendor

sample	$^{49}\text{Ti}/^{48}\text{Ti}$	1 sig error
Zr-2 foil	0.07397	0.00032
Zr-4 foil	0.07459	0.00123
Tel Zr-4	0.07412	0.00126
Tel Zr-2	0.07478	0.00081
LSA C3	0.09539	0.00157
SUS33C	0.09796	0.00244
SUS23A	0.10342	0.00511
LSA A4	0.10789	0.00026

Note: ratios for each sample are average of 8 to 20 different analyses

The remaining samples will undergo SIMS analysis for  $^{49}\text{Ti}/^{48}\text{Ti}$  ratios and all samples will also be analyzed for Hf isotope ratios, to further determine usefulness of Hf isotope ratios previously measured in the vendor-supplied Zr-2 and Zr-4 samples. Later, we hope to identify and analyze (by SIMS) additional impurity elements in both the non-irradiated samples and the irradiated samples. Amounts remaining from the fuel vendor samples should be more than adequate for future work due to the very small volumes and masses of sample needed for SIMS analyses.

## 2.3 Energy Production Estimates

In order to infer the energy production of the fuel adjacent to a channel sample, the titanium isotope ratios within the channel must be calculated as a function of burnup. However, since no detailed fuel design or operational data was available, the reactor modeling efforts have been restricted to simple pin-cell calculations based on a generic 8x8 BWR bundle design. The pin-cell was modeled with six radial regions to account for the fuel, cladding, coolant, fuel channel and inter-bundle water. The assumptions used for the pin-cell calculation are listed in Table 2.

**Table 2.** Generic 8×8 BWR Bundle

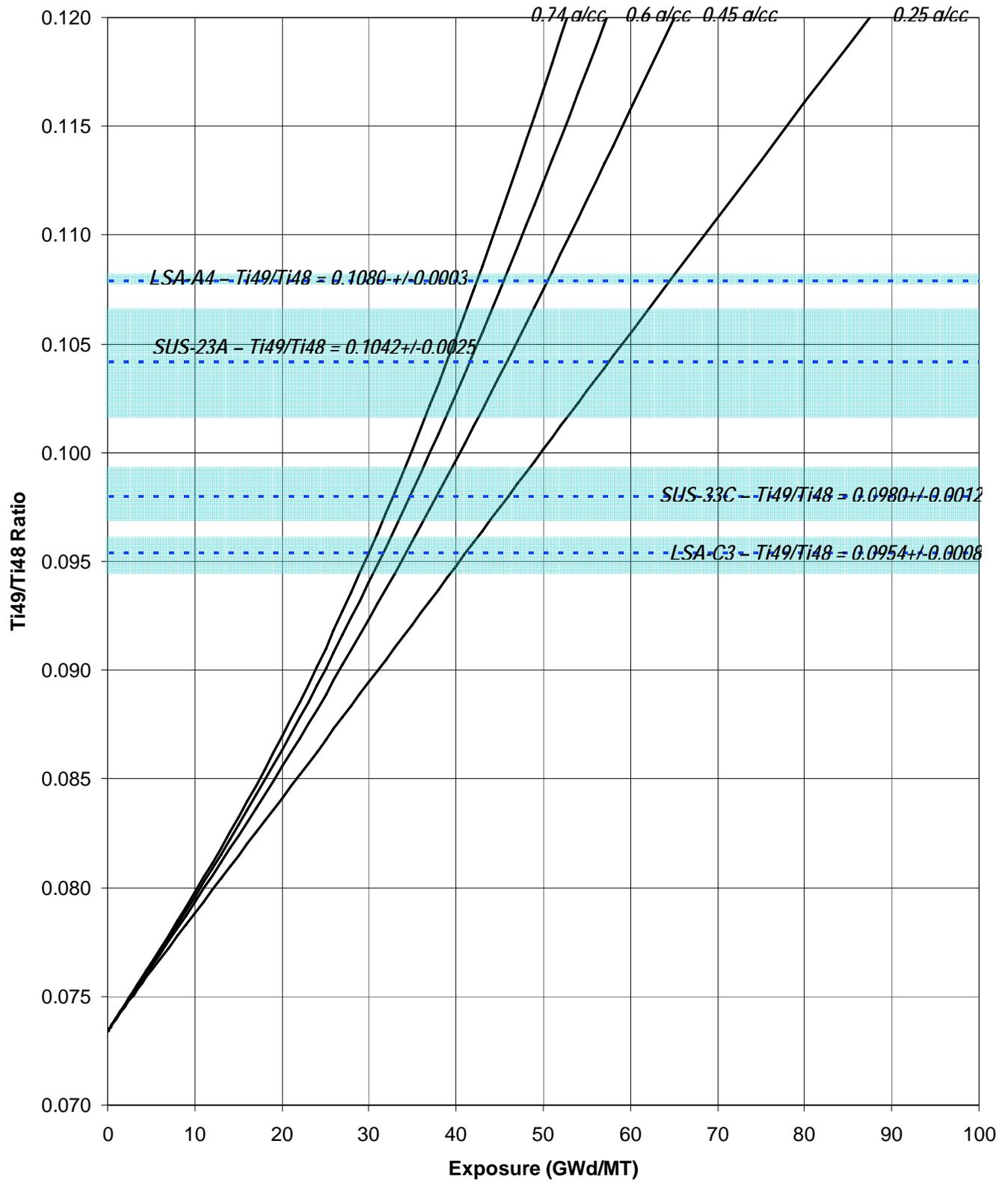
<b>Parameter</b>	<b>Value</b>
UO <sub>2</sub> Density	10.28 g/cc
<sup>235</sup> U Enrichment	3.0%
Fuel Radius	0.528 cm
Cladding Radius	0.626 cm
Coolant Radius	0.917 cm
Channel Radius	0.946 cm
Outer Radius	0.989 cm
Fuel Temperature	1000 K
Clad Temperature	600 K
Coolant Temperature	550 K
Channel Temperature	550 K
Coolant Density Range	0.25-0.74 g/cc
Exposure Range	0-70,000 MWd/MT

Figure 1 shows the calculated  $^{49}\text{Ti}/^{48}\text{Ti}$  ratio as a function of fuel burnup for four different water densities (the corresponding range of void fractions is 0 to 0.7). The curve starts at the natural ratio of 0.0734 and increases with burnup as  $^{48}\text{Ti}$  is converted to  $^{49}\text{Ti}$ . The mean  $^{49}\text{Ti}/^{48}\text{Ti}$  ratios for the four samples that have been analyzed are shown as dashed blue lines surrounded by light blue regions that correspond to a  $\pm 1$  sigma error bound.

In the absence of a known axial power shape, the burnup estimates should be regarded as local as opposed to bundle average. The results are strongly dependent on the coolant density. This indicates that detailed knowledge of the void history of the sample location will be needed for accurate burnup estimates.

---

<sup>1</sup> Using WIMS-8 – “WIMS – A Modular Scheme for Neutronics Calculations,” ANSWER/WIMS(99)9, The ANSWERS Software Package, AEA Technology.



**Figure 1.** Calculated and measured  $^{49}Ti/^{48}Ti$  ratios as a function burnup

Table 3 lists the estimated local burnup for the fuel bundle adjacent to each sample location for the minimum and maximum coolant densities. Since it is believed that the samples came from near the bottom of the channel, the 0.74g/cc results are probably more realistic. Again, it must be stressed that these calculations and burnup estimates are preliminary. More accurate calculations will be completed when detailed fuel design information becomes available. However, the overall range of possible burnup is reasonable.

**Table 3.** Estimated fuel burnup at the sample locations assuming 0.74g/cc coolant

<b>Sample ID</b>	<b>Ti49/Ti48</b>	<b>Estimated MWd/MT at 0.25g/cc</b>	<b>Estimated MWd/MT at 0.74g/cc</b>
LSA C3	0.09539	41.0	30.0
SUS 33C	0.09796	46.0	32.8
SUS 23A	0.10416	57.5	39.0
LSA A4	0.10789	65.5	42.4

### 3.0 References

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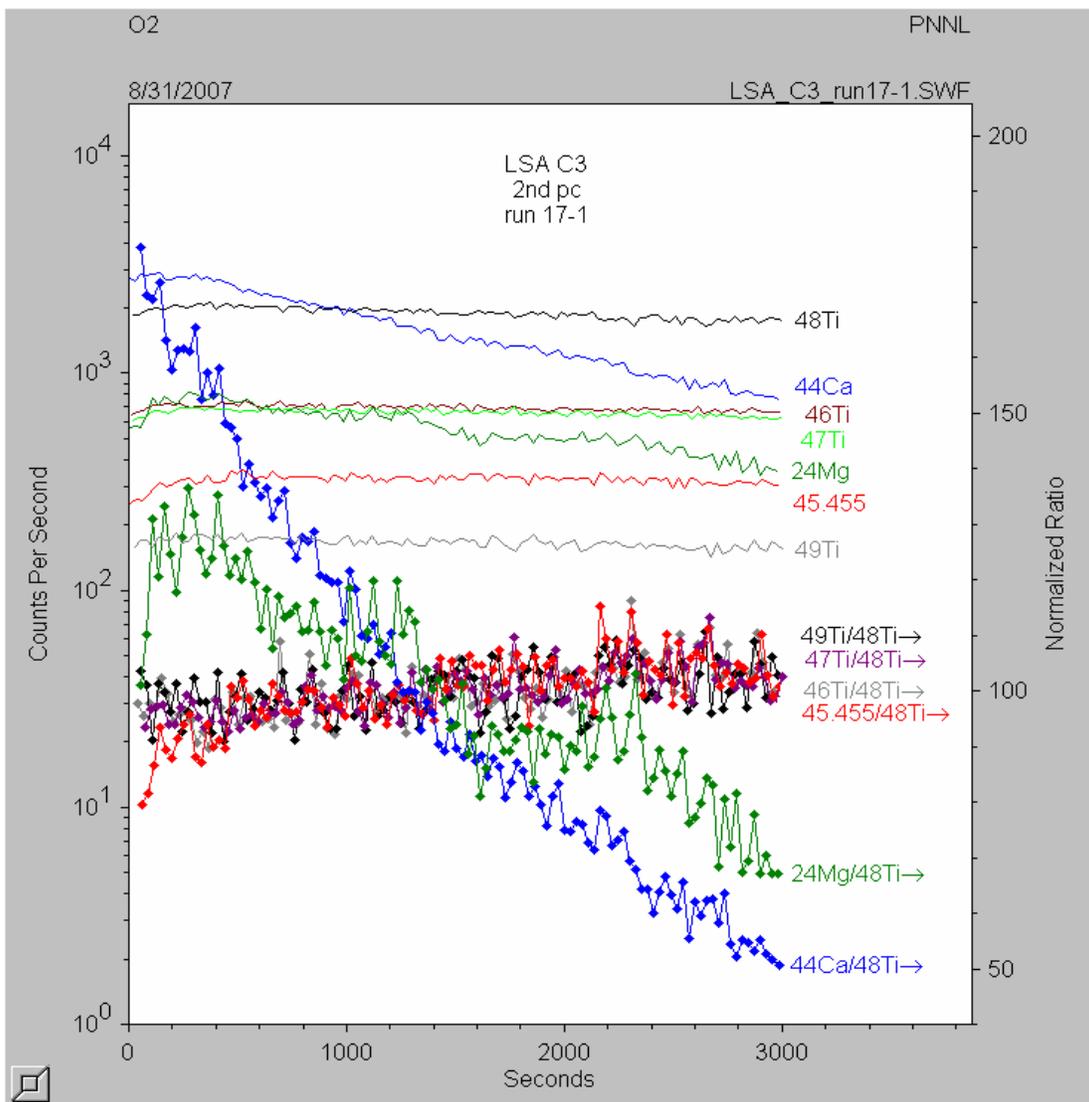
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## **APPENDIX A**

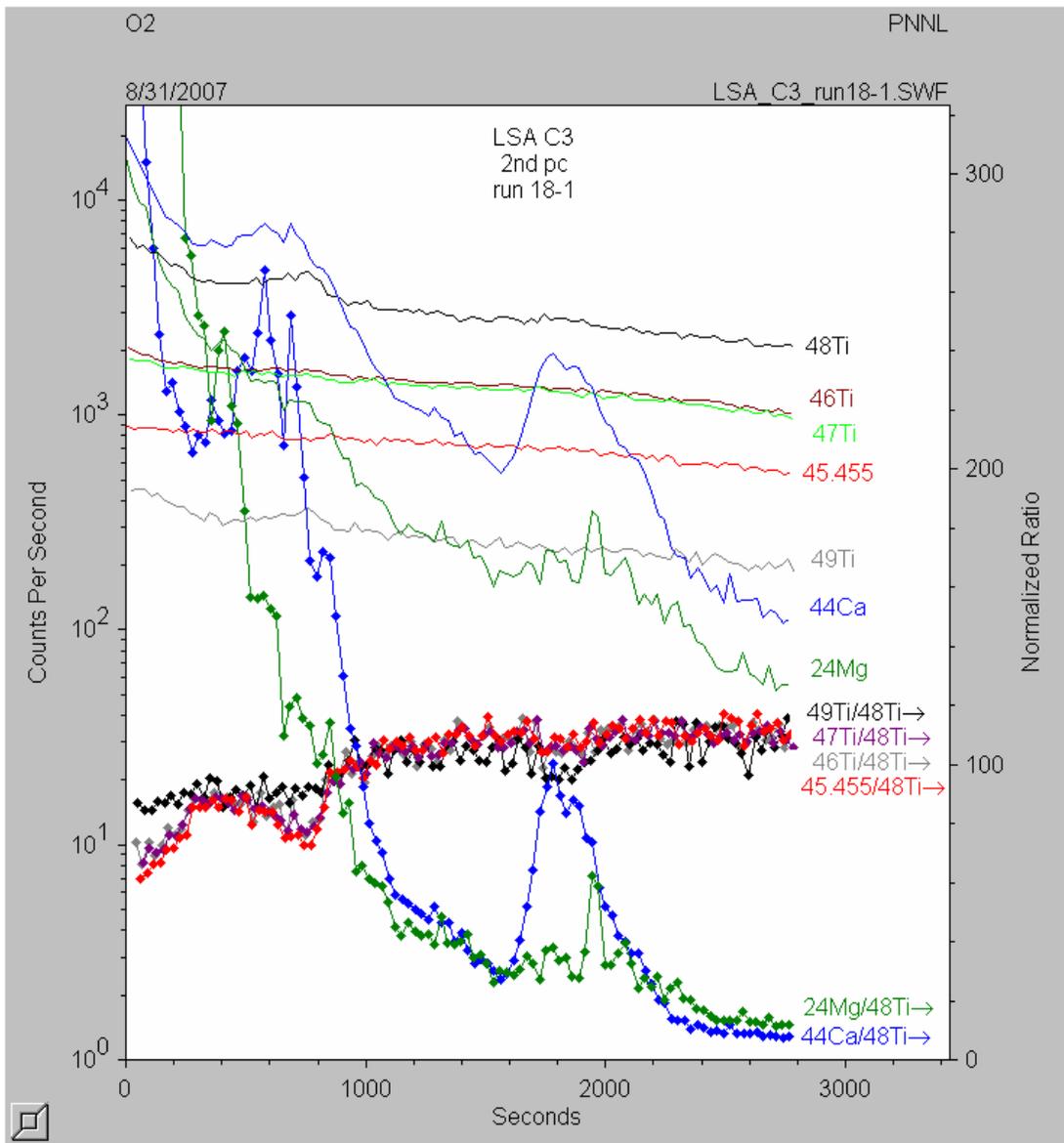
### **Gamma Analysis Data and Examples of SIMS Analyses**

# APPENDIX A: Gamma Analysis Data and Examples of SIMS Analyses



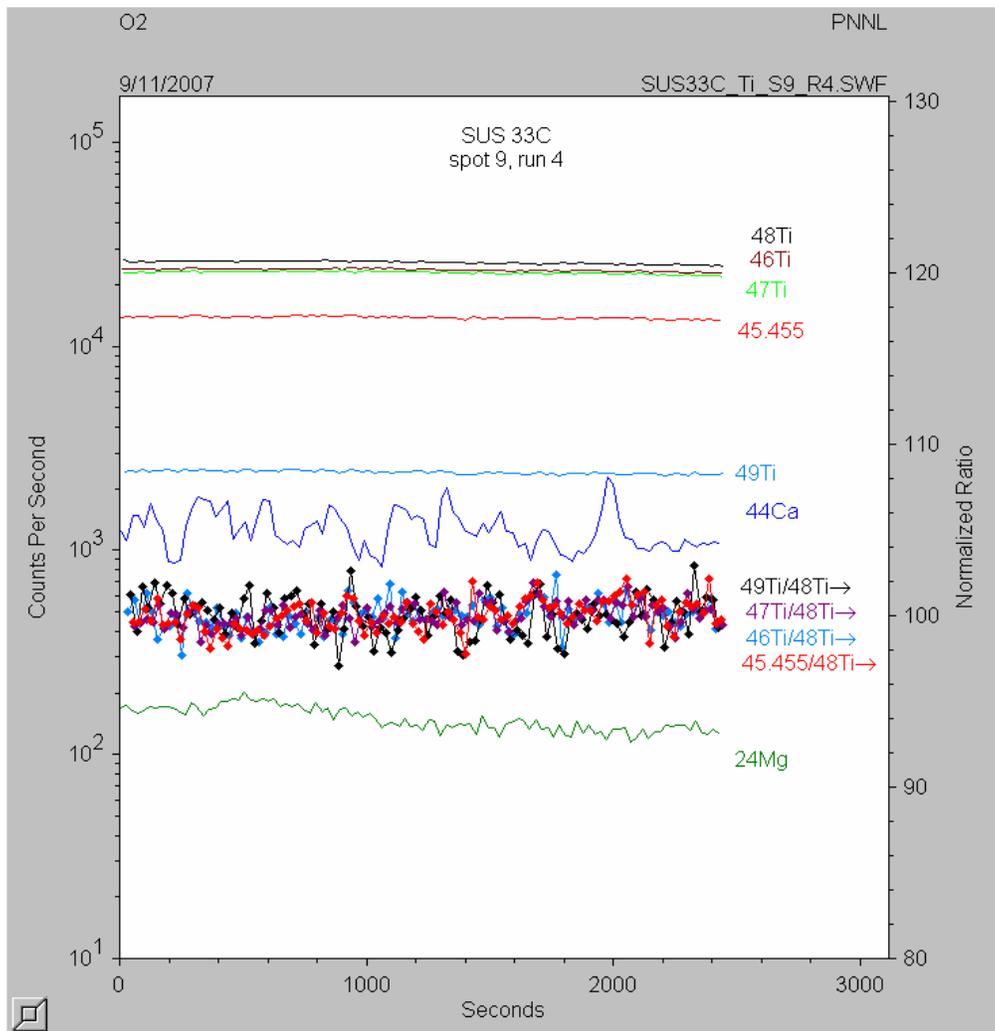
**Figure A.1** An example of ion signals and ratio measurements during presputtering analyses.

The left scale give ion count rates as indicated for the various ions measured (simple colored lines), and the right scale indicates the % change in ratios relative to a running average and up to that measurement cycle or point in time, for the various ratios all normalized to ion counts at mass 48 (colored lines with dot symbols). As the Ca ions decrease, the ratios normalized to mass 48 increase slightly over time, due to the decreasing contributions from  $^{48}\text{Ca}$  ions.



**Figure A.2** Ion signals and ratio measurements displaying impurities

A similar plot as in Figure A.1, displaying brief increases in impurity Ca and Mg ion signals possibly indicating an impurity inclusion at some depth in the irradiated Zr alloy sample.



**Figure A.3** Stable SIMS analysis of a clean, uncontaminated sample

An example of a good stable SIMS analysis run obtained after removal of surface contamination and lacking inclusions or apparent contamination at depth.

**Table A.1** Results of gamma counting analyses of irradiated fuel vendor samples

Customer Sample ID	Analysis Method	Analyte	Result (pCi)	2 Sigma Uncertainty	detection limit	Analysis Date
LSA A3 TEM	EPA901.1	CO-58	1.33E+05	2.84E+04	4.44E+04	08/01/07
LSA A4 TEM	EPA901.1	CO-58	1.83E+05	3.12E+04	4.77E+04	07/31/07
SUS 23A TEM	EPA901.1	CO-58	8.49E+04	2.18E+04	3.45E+04	08/01/07
SUS 33A TEM	EPA901.1	CO-58	6.61E+04	1.86E+04	2.93E+04	08/01/07
SUS 33C TEM	EPA901.1	CO-58	5.17E+04	1.80E+04	2.88E+04	08/01/07
		<b>Total pCi CO-58</b>	<b>5.19E+05</b>			
LSA A3 TEM	EPA901.1	CO-60	3.76E+06	1.67E+05	4.63E+04	08/01/07
LSA A4 TEM	EPA901.1	CO-60	3.10E+06	1.40E+05	5.10E+04	07/31/07
LSA C1 TEM	EPA901.1	CO-60	1.40E+06	6.60E+04	2.49E+04	08/01/07
LSA C3 TEM	EPA901.1	CO-60	1.39E+06	6.54E+04	2.18E+04	08/01/07
SUS 23A TEM	EPA901.1	CO-60	2.56E+06	1.16E+05	3.62E+04	08/01/07
SUS 23C TEM	EPA901.1	CO-60	4.22E+06	1.86E+05	4.55E+04	08/01/07
SUS 33A TEM	EPA901.1	CO-60	2.29E+06	1.05E+05	3.58E+04	08/01/07
SUS 33C TEM	EPA901.1	CO-60	2.95E+06	1.32E+05	3.28E+04	08/01/07
		<b>Total pCi CO-60</b>	<b>2.17E+07</b>			
LSA C3 TEM	EPA901.1	CR-51	2.81E+06	3.36E+05	3.96E+05	08/01/07
SUS 23A TEM	EPA901.1	CR-51	4.83E+06	5.62E+05	6.53E+05	08/01/07
SUS 23C TEM	EPA901.1	CR-51	5.44E+06	6.02E+05	6.63E+05	08/01/07
SUS 33A TEM	EPA901.1	CR-51	4.23E+06	5.00E+05	5.86E+05	08/01/07
SUS 33C TEM	EPA901.1	CR-51	4.24E+06	5.26E+05	6.45E+05	08/01/07
		<b>Total pCi CR-51</b>	<b>2.16E+07</b>			
LSA A3 TEM	EPA901.1	MN-54	2.93E+06	1.57E+05	5.48E+04	08/01/07
LSA A4 TEM	EPA901.1	MN-54	2.84E+06	1.52E+05	5.28E+04	07/31/07
LSA C1 TEM	EPA901.1	MN-54	3.75E+05	2.44E+04	1.71E+04	08/01/07
LSA C3 TEM	EPA901.1	MN-54	4.48E+05	2.94E+04	2.30E+04	08/01/07
SUS 23A TEM	EPA901.1	MN-54	2.06E+06	1.12E+05	4.18E+04	08/01/07
SUS 23C TEM	EPA901.1	MN-54	2.29E+06	1.23E+05	4.45E+04	08/01/07
SUS 33A TEM	EPA901.1	MN-54	1.85E+06	1.00E+05	3.49E+04	08/01/07
SUS 33C TEM	EPA901.1	MN-54	1.95E+06	1.06E+05	4.25E+04	08/01/07
		<b>Total pCi MN-54</b>	<b>1.47E+07</b>			
LSA A3 TEM	EPA901.1	NB-95B	6.08E+07	2.80E+06	9.74E+04	08/01/07
LSA A4 TEM	EPA901.1	NB-95B	5.04E+07	2.32E+06	9.84E+04	07/31/07
SUS 23A TEM	EPA901.1	NB-95B	1.39E+07	6.42E+05	5.05E+04	08/01/07
SUS 23C TEM	EPA901.1	NB-95B	2.05E+07	9.48E+05	6.47E+04	08/01/07
SUS 33A TEM	EPA901.1	NB-95B	1.06E+07	4.92E+05	4.49E+04	08/01/07
SUS 33C TEM	EPA901.1	NB-95B	1.55E+07	7.20E+05	5.35E+04	08/01/07
		<b>Total pCi NB-95B</b>	<b>1.72E+08</b>			
LSA A3 TEM	EPA901.1	SB-125	1.38E+08	7.60E+06	4.32E+05	08/01/07
LSA A4 TEM	EPA901.1	SB-125	1.36E+08	7.48E+06	3.81E+05	07/31/07
LSA C1 TEM	EPA901.1	SB-125	6.17E+07	3.40E+06	1.70E+05	08/01/07
LSA C3 TEM	EPA901.1	SB-125	6.61E+07	3.64E+06	1.86E+05	08/01/07
SUS 23A TEM	EPA901.1	SB-125	1.13E+08	6.20E+06	2.86E+05	08/01/07
SUS 23C TEM	EPA901.1	SB-125	1.32E+08	7.26E+06	3.22E+05	08/01/07
SUS 33A TEM	EPA901.1	SB-125	1.06E+08	5.80E+06	2.57E+05	08/01/07
SUS 33C TEM	EPA901.1	SB-125	1.07E+08	5.86E+06	2.59E+05	08/01/07
		<b>Total pCi SB-125</b>	<b>8.60E+08</b>			
LSA A3 TEM	EPA901.1	SN-113	1.02E+07	6.14E+05	1.58E+05	08/01/07
LSA A4 TEM	EPA901.1	SN-113	1.00E+07	6.02E+05	1.64E+05	07/31/07
SUS 23A TEM	EPA901.1	SN-113	4.84E+06	2.99E+05	1.30E+05	08/01/07
SUS 23C TEM	EPA901.1	SN-113	5.58E+06	3.43E+05	1.34E+05	08/01/07
SUS 33A TEM	EPA901.1	SN-113	4.14E+06	2.62E+05	1.42E+05	08/01/07
SUS 33C TEM	EPA901.1	SN-113	4.68E+06	2.90E+05	1.29E+05	08/01/07
		<b>Total pCi SN-113</b>	<b>3.94E+07</b>			
LSA A3 TEM	EPA901.1	ZR-95	2.54E+07	1.54E+06	1.77E+05	08/01/07
LSA A4 TEM	EPA901.1	ZR-95	2.15E+07	1.31E+06	1.76E+05	07/31/07
SUS 23A TEM	EPA901.1	ZR-95	5.97E+06	3.70E+05	9.59E+04	08/01/07
SUS 23C TEM	EPA901.1	ZR-95	8.93E+06	5.48E+05	9.28E+04	08/01/07
SUS 33A TEM	EPA901.1	ZR-95	4.58E+06	2.85E+05	7.63E+04	08/01/07
SUS 33C TEM	EPA901.1	ZR-95	6.75E+06	4.16E+05	8.54E+04	08/01/07
		<b>Total pCi ZR-95</b>	<b>7.31E+07</b>			

## **APPENDIX B**

### **Secondary Ionization Mass Spectrometric (SIMS) Analysis of Zircalloys, Background Information and General Approaches Taken**

# Appendix B: Secondary Ionization Mass Spectrometric (SIMS) Analysis of Zircaloys, Background Information and General Approaches Taken

## B.1 SIMS Background

Secondary ionization mass spectrometry (SIMS) analysis is a mature and highly successful analytical method, is usually conducted directly on samples with little or no preparation or separation chemistry, and offers advantages of quick turnaround compared to other mass spectrometric analysis methods requiring time- and labor-intensive preparation. SIMS analysis employs a focused beam of high-energy primary ions directly bombarding the sample surface to sputter the sample and is capable of high spatial resolution compared to laser ablation. Transfer of energy and momentum results in ejection of neutral and charged particles (ions to complex molecules), and this ejection or removal is called sputtering.

In further contrast to other mass spectrometric analysis methods, SIMS is capable of microscopic physical spatial resolution in addition to elemental or isotopic analysis. This is due both to the spatial resolution afforded by using a primary ion beam for initial sputtering and the secondary ion optics. Some ion beams can sample small areas down to 1 micron in diameter, a much smaller spot size than achievable by laser ablation. A typical SIMS instrument is designed with astigmatic spherical ion optics so that relative positions of all secondary ions from a given area on the sample surface are preserved when reaching an ion imaging detector. Spatial resolution provided by SIMS results in analysis of microscopic features in a sample material or microscopic objects, and evaluation of microscopic elemental and isotopic heterogeneity in a very small area (micron-scale) with either ion counting detectors or ion imaging detectors.

**The detection efficiency for SIMS is comparable to, or better than most,** other mass spectrometers, but may vary with element and the sample matrix containing the element of interest. The amount of sample consumed by the SIMS primary ion beam may be very small, less than a few cubic microns. Production of secondary ions from a sample depends to a large extent on the electron affinity (for negative ions) and the first ionization potential (for positive ions) of the element of interest. Sample matrix effects in SIMS analysis can affect secondary ionization of the element and concentration determinations, and matrix-matched standards are usually employed. Matrix effects must be accounted for when measuring inter-element ratios such as U/Th, but are of little concern for analysis of isotope ratios. As in other mass spectrometers, molecular and isobaric interferences must be avoided or considered during SIMS analysis.

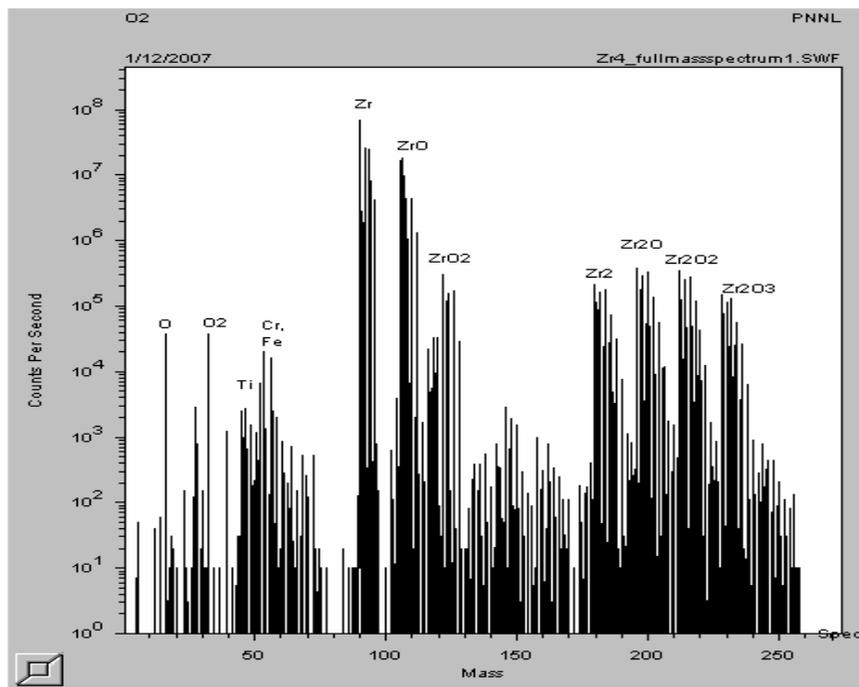
## B.2 SIMS Approaches for Analysis of Zircaloy Samples

The project goal is to validate the changing isotope ratios of selected impurity elements in irradiated versus natural or unirradiated Zircaloy samples as a signature for reactor history and operation. The Zircaloy sample matrix allows for high efficiency sputtered ion yields, providing excellent detection capability with minimal sample consumption. Of practical importance is that minimal sample sizes may be utilized to reduce levels of radiation during handling, transfer, and analysis of irradiated samples.

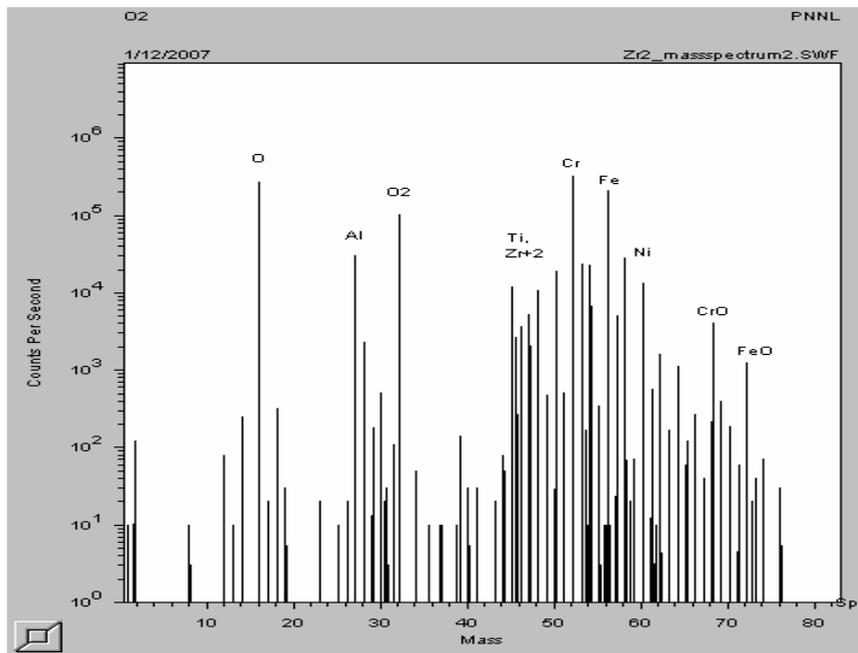
Zircaloy-2 (Zr-2) consists of 98.25 weight % zirconium with 1.45% tin, 0.10% chromium, 0.135% iron, 0.055% nickel and 0.01% hafnium. Other sources specify Zircaloy-2 as zirconium with 1.20–1.70% tin,

0.07–0.20% iron, 0.05–0.15% chromium, and 0.03–0.08% nickel, with tin content at the lower and the iron/chromium/nickel content at the higher end of the specification. Zircaloy-4 (Zr-4) consists of 98.23 weight % zirconium with 1.45% tin, 0.21% iron, 0.1% chromium, and 0.01% hafnium. Two additional samples in this study are ZrNb alloys, where the Zr is replaced by 2.5 to 3% Nb

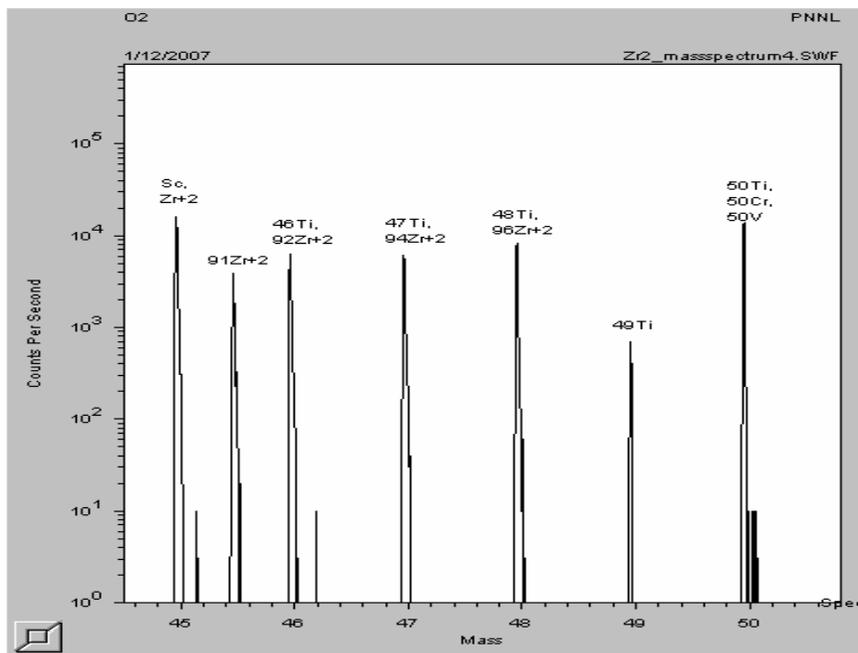
Initial studies were conducted on ‘cold’ samples. A total of six samples of different Zircalloys were obtained from PNNL colleagues and from Teledyne’s Wah Chang (Albany , Oregon). Scans of the mass spectrum were done on samples to determine the presence of impurity elements and to assess molecular interferences arising from interactions of sample matrix elements (Zr, Nb mainly) with the SIMS primary ion beam ( $O_2^+$  ions were used).. Several examples are shown in Figures B.1–B.33, beginning with an overall scan from H to Pu, and ending with a scan more focused on the Ti isotope mass range.



**Figure B.1** SIMS Mass Scan from H to >Pu Mass Range, Showing Matrix Elements (Zr), and Major Interferences Arising from Zr and the SIMS Primary Oxygen Ion Beam



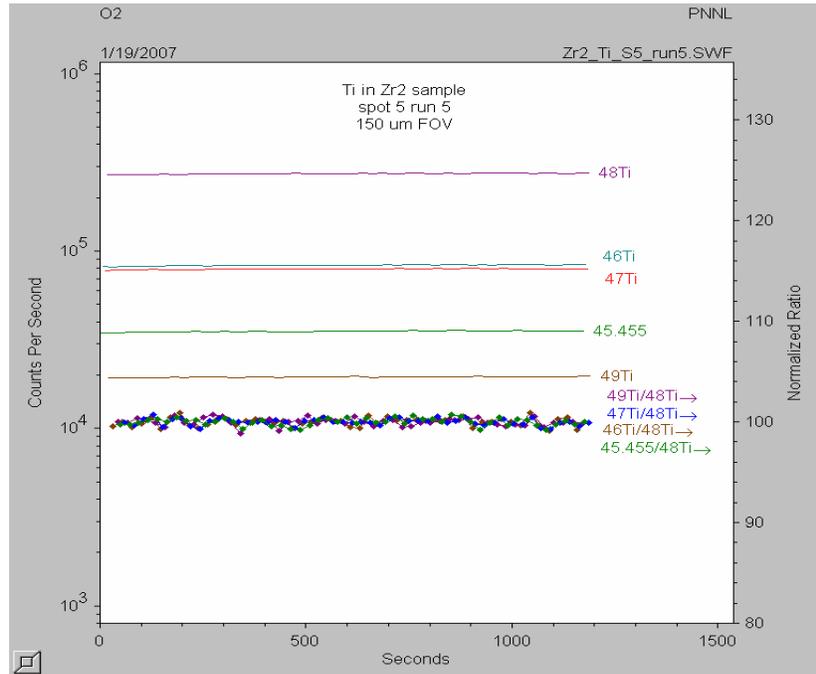
**Figure B.2** SIMS Mass Scan from H through Transition Metals. Chromium, Fe, and Ni are major constituents.



**Figure B.3** SIMS Mass Scan from Sc to Ti, Showing Ti Masses and Zr<sup>+2</sup> Interferences

### B.3 SIMS Measurement of Ti and Hf Isotope Ratios in Irradiated Zircaloy Samples

Because it varies strongly with irradiation, is reasonably easy to resolve using the SIMS technique, the most useful isotope ratio identified so far for determining irradiation levels is  $^{49}\text{Ti}/^{48}\text{Ti}$ . Previous project work at PNNL revealed that titanium is a useful impurity to study when looking for fluence indicators; the ranges of neutron fluence exposure and fuel burnup wherein this ratio is useful was also determined (Reid et al. 2001). Other Ti isotopes (e.g.,  $^{46}\text{Ti}/^{48}\text{Ti}$ ,  $^{47}\text{Ti}/^{48}\text{Ti}$ ) change much more slowly with burnup and are not very useful, or have isobaric interference with other impurity elements ( $^{50}\text{Ti}$  vs.  $^{50}\text{V}$  vs.  $^{50}\text{Cr}$ ). This latter type of interference is shown in Figure 3, and additional interferences arising from doubly charged Zr ions present at mass 46, 47, and 48. The  $^{91}\text{Zr}^{+2}$  interference gives rise to a very constant and stable ion signal occurring at an easily resolved half-mass position. This interference is included in each analysis to correct the  $^{48}\text{Ti}$  ion count rate by subtracting the signal from the doubly charged  $^{96}\text{Zr}^{+2}$  ions (which have the same charge-to-mass ratio). A graphical example of a single Ti isotope ratio SIMS analysis is shown in Figure B.4.



**Figure B.4** Typical SIMS Isotope Ratio Data Acquisition for Ti Isotopes, with  $^{91}\text{Zr}^{+2}$  Ions Included (mass 45.455), and Excluding Ions at Mass 50, due to Cr and V Interferences

In this example (Figure B.4), the ion count rates for various Ti isotopes (left-hand y axis) are shown along with the ion count rate for the half-mass  $^{91}\text{Zr}^{+2}$  interference. All Ti ion count rates except for  $^{49}\text{Ti}$  are higher due to other  $\text{Zr}^{+2}$  interferences, e.g.,  $^{92}\text{Zr}^{+2}$  at mass 46, etc. (Both zirconium 91 and zirconium 96 were present in the sample and each presents its own interference.) The lower plots with connected data points show cycle-by-cycle isotope ratios normalized (%) to a cumulative running average for each ratio (right-hand y axis) during the run and illustrate how stable the signals are, even with the interferences.

The Zr isotope ratios were analyzed separately from Ti isotope ratios in several samples to measure possible mass bias effects on the Zr ratios. Assuming natural starting Zr isotope ratios, the measured mass bias was also applied in calculating the ion count rates due to the  $Zr^{+2}$  interferences in the Ti mass range, which were then subtracted to correct the Ti ion count rates, especially for the interference  $^{96}Zr^{+2}$  affecting  $^{48}Ti$  ion counts. A total of five spots were pre-sputtered in each of the six various Zircaloy samples, and several Ti isotope ratio acquisitions taken in each spot, as in the example above.

As demonstrated in the following table, the magnitude of the correction on the  $^{48}Ti$  ion count rate is substantial in most samples, but the corrected  $^{49}Ti/^{48}Ti$  ratios are within 0.7% between the various samples, and all are close to the natural value for  $^{49}Ti/^{48}Ti$ , which is 0.0745. The apparent difference in the measured values below and the natural value is a typical difference termed instrument measurement or mass bias apparent in most types of mass spectrometric analysis and arises from specific instrument design parameters, fundamental elemental properties, and specifically in SIMS, slight differences in ion energies and sputtering yields. (The statistical approach to the corrections will be discussed in an upcoming report.)

One of the samples (Zr2) displays less difference between uncorrected and corrected  $^{49}Ti/^{48}Ti$  ratios, and this indicates that this sample is higher in Ti impurity than the other five samples. The absolute contents of Ti and other impurity elements do not affect isotope ratios measurements unless the contents are altogether too low to obtain ion count rates for desired measurement precision and accuracy. Thus far, the Ti contents in these six representative samples were adequate for good measurement and good reproducibility, as shown in Table B.1.

**Table B.1** Uncorrected and Corrected SIMS  $^{49}Ti/^{48}Ti$  Ratios in 6 Samples of Zircaloy

Sample	Ti 49/48, Average (as measured) <sup>(a)</sup>	2 SE	Ti 49/48 Average, Corrected	2 SE, Corr
Zr2	0.07108	7.06E-04	0.07376	1.29E-04
Zr4	0.06317	7.33E-04	0.07372	7.38E-05
TelZr4	0.06185	1.66E-03	0.07353	1.45E-04
TelZr2	0.05739	8.46E-04	0.07328	1.51E-04
TelZrNb2.5	0.06463	1.16E-03	0.07362	1.31E-04
TelZrNb3	0.06775	1.09E-03	0.07364	1.84E-04

(a) As measured ratio before correction for  $^{96}Zr^{+2}$  interference.

SIMS analysis can also be used to measure impurity element abundances in most sample matrices, using different analytical settings and either using matrix-matched standards or some reasonable assumptions. Analyses are underway to determine approximate contents of Ti and a few selected impurity elements in the six Zircaloy samples with the goal of finding additional species that could be useful in determining

irradiation levels, and to determine minimum impurity element contents for successful isotope ratio measurements.

#### **B.4 Preliminary Measurements of Ti isotope Ratios in Irradiated Zircaloy**

Irradiated sample studies will be discussed in much greater detail in a subsequent deliverable, however the opportunity to analyze a sample presented itself and so the analysis was performed. A sample of irradiated Zircaloy-4 used in a tritium-producing target was available at PNNL and was assessed for measurement suitability. The level of radioactivity from one or more gamma emitters and the level of tritium in the sample, even after vacuum furnace treatments, was high relative to allowed limits for radioactive samples on the PNNL SIMS instrument. This required subdividing the sample into smaller portions for analysis. The sample was also somewhat brittle and friable, and we needed to devise a way of mounting very small pieces, approximately 50 microns in the longest dimension. To this end, only one sample at a time could be pressed into high purity indium metal, which is relatively soft and would form a conductive matrix when mounted into a typical SIMS sample holder. This sample mounting method required a high-powered optical microscope and a high-precision micromanipulator to track the microscopic sample piece and place it in position for mounting in the indium metal.

The small portion of sample was easily located by moving the SIMS sample stage around until a strong Zr ion signal was found. Ion imaging detectors helped delineate the shape of the exposed sample piece and to precisely position the piece for analysis. The high purity Indium (In) appeared to have no measurable Ti, but to avoid ambiguities in measurements, SIMS settings were adjusted to select only ions from a small 10- or 25-micron-sized ion aperture, guided by using a real-time Zr ion image. The small piece was consumed in approximately 1 to 1.5 days' analysis time, and other sample pieces will be analyzed in the near future. A number of analyses were conducted on the sample piece, with some  $^{49}\text{Ti}/^{48}\text{Ti}$  ratios definitely reflecting an irradiation effect, and others trending toward natural, possibly indicating some contamination with natural Ti during handling and mounting.