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Characterization of Dissolved High-Burnup Nuclear Fuel with Microcalorimeter, High-Purity Germanium, and Cadmium Zinc Telluride Gamma Spectroscopy

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Abstract
Nondestructive characterization of high-burnup nuclear fuels is an important potential application of gamma spectroscopy and enabling technology for advanced reactors and fuel cycle facilities. While this is a challenging measurement due to the complexity of the gamma spectrum and severe Compton scattering background from intense fission product activity, new technologies such as microcalorimeter gamma spectrometers may be able to access additional signatures of fuel composition. To evaluate the potential of advanced and traditional gamma spectroscopy in characterizing spent fuel composition, burnup, and cooling time we conducted a series of measurements on dissolved high-burnup light water reactor fuels using microcalorimeter, high-purity germanium, and cadmium zinc telluride detectors. In particular, microcalorimeter and high-purity germanium detectors were found to be complementary in that each provide the best available energy resolution in low- and high-energy regions of the spectrum respectively. In the low-energy part of the spectrum below 200 keV, we find that additional burnup and cooling time indicators are available with microcalorimetry beyond the traditional $^{134}Cs/^{137}Cs$ ratio. $^{243}Am/^{241}Am$ is most sensitive to burnup and $^{155}Eu/^{154}Eu$ is sensitive to both cooling time and burnup. These ratios may provide more robust analysis of burnup and cooling time especially in combination with the $^{134}Cs/^{137}Cs$ ratio from a germanium detector. We will present results from this study and discuss implications for safeguards and material accounting in advanced reactors and nuclear fuel cycle facilities.

Introduction
The goal of this measurement campaign is to provide the first comparison of nondestructive isotopic analysis performance between traditional and advanced gamma spectroscopy technologies for liquid-form irradiated fuel samples. While available samples of irradiated fuel salt are extremely limited at the present time, dissolved samples of high-burnup light water reactor fuels can answer important questions about what signatures may be measurable in the future application of on-line molten salt reactor safeguards.

Gamma Spectroscopy Technologies

Three primary technologies were selected for evaluation (Table 1). Cadmium zinc telluride (CZT) provides medium energy resolution and detection efficiency in an extremely compact package due to its room-temperature operation. The Ritec μSPEC500 (Figure 1, left) was selected as a representative CZT detector with a moderate crystal size of 500 mm^3 and reasonable observed energy resolution. High-purity germanium (HPGe) provides high energy resolution and high detection efficiency. The Ortec IDM-200-P (Figure 1 center, similar to a Detective EX) was selected due to its large crystal which provides good efficiency particularly for high-energy gamma rays resulting from fission products. The IDM-200-P is electrically cooled and suitable for use in a wide range of locations. Its energy resolution is not as good as that of smaller germanium detectors, so samples were also measured on a low-energy germanium (LEGe) detector. Microcalorimetry provides ultra-high energy resolution with moderate detection efficiency in the energy range from approximately 15-300 keV. The SOFIA microcalorimeter gamma spectrometer (Figure 1 right) is the first instrument of its type designed to be deployed to nuclear facilities and analytical laboratories and is much more easily moved to a new location than other microcalorimeter systems [1]. Oak Ridge National Laboratory provided the CZT and HPGe detectors, and Los Alamos National Laboratory provided the SOFIA microcalorimeter system. Measurements were performed at Oak Ridge National Laboratory.

Type	**Model**	**Detection Volume**	**Observed FWHM at 123 keV**	**Observed FWHM at 662 keV**
CZT	Ritec μSPEC500	500 mm^3 quasi hemispherical CZT	4.9-5.3 keV	8.1-8.4 keV
HPGe	Ortec IDM-200-P	85 mm diameter x 30 mm length P-type HPGe	1.63-1.70 keV	2.02-2.12 keV
HPGe	Canberra GC2518	62 mm diameter x 35.5 mm HPGe	1.03-1.07 keV	1.45-1.47 keV
microcalorimeter	SOFIA	256 superconducting transition-edge sensors with 1.5x1.5x0.4 mm Sn absorbers	0.06-0.11 keV	(outside of energy range)

Table 1: Summary of gamma spectroscopy technologies evaluated.

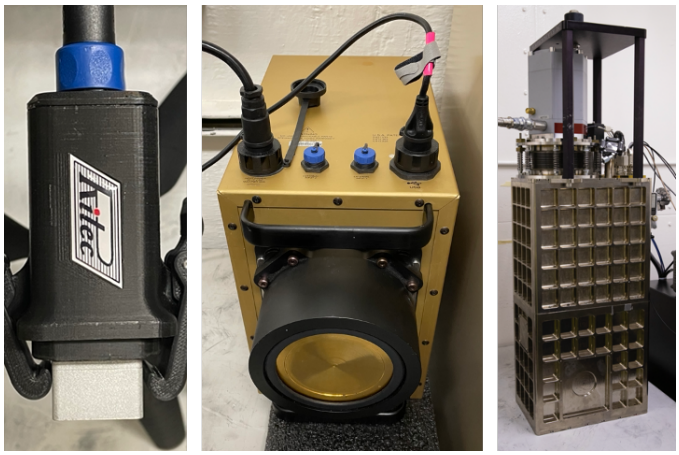

Figure 1: (Left) Ritec µSPEC500 cadmium-zinc-telluride detector; (center) Ortec IDM-200-P high-purity germanium detector; (right) SOFIA microcalorimeter instrument.

Sample Preparation

Five solutions of dissolved nuclear fuel were selected from the analytical laboratory inventory and prepared in a consistent geometry for gamma spectroscopy measurements. Table 2 summarizes the samples which were chosen to represent a range of burnup and cooling time. Each starting solution was characterized through destructive analysis. Based on the measured ^{137}Cs concentration from this previous work, the sample mass required to provide 5 MBq of ^{137}Cs was determined. The required sample solution mass was then diluted with clean 2% nitric acid to bring the total solution volume to 1.5 mL in order to provide a consistent geometry for gamma measurements. Additionally, a Standard Reference Source solution (124240) was procured from Eckert & Ziegler to provide an energy and efficiency calibration reference. A 1.5 mL quantity of the standard solution was used directly in its original concentration. Each 1.5 mL unit of solution was sealed in a plastic vial within a larger plastic scintillation vial, which was placed in a plastic bag for handling (Figure 2).

Sample ID	**Burnup (GWd/MTU)**	**Discharge Date (year)**	**Solution Mass (g)**	**Gamma Dose Rate(mrem/hr)**	**Beta Dose Rate (mrad/hr)**
SR-35-2402A	65.5	1989	0.4222	16	2628
SR-1450C	65.4	2000	0.3456	18	2619
SR-215A	46.9	2010	0.2502	22	3501
SR-240A	44.7	1994	0.3754	16	3528
SR-0165A	38.8	1994	0.4375	20	3570
124240	Gamma standard solution containing Pb-210, Am-241, Cd-109, Co-57, Ce-139, Hg-203, Sn-113, Sr-85, Cs-137, Y-88, Co-60				

Table 2: Summary of measured samples. Each sample consisted of 1.5 mL total solution volume. Clean 2% nitric acid was added to the initial solution mass given in the table to bring the total volume to 1.5 mL except for the standard solution 124240 which was used at its original concentration. Dose rates were measured at contact on the inner plastic vial.

Figure 2: Samples prepared for gamma measurements consisted of 1.5 mL total solution volume in a plastic vial, overpacked in a plastic scintillation vial and plastic bag. Image on left shows empty vials for reference.

Measurements

CZT, HPGe, and microcalorimeter detectors were set up together for simultaneous measurements on each sample (Figure 3). Samples were placed in a plastic stand with the CZT and microcalorimeter detectors in close proximity. The HPGe detector, with its relatively large crystal and much higher detection efficiency, was placed approximately 28 cm from the sample in order to limit its dead time. The high activity of the samples provided a test of count rate capability and dose tolerance for each detector type.

After acquisition, HPGe spectra were energy calibrated with a second-order polynomial fit to 59.5, 123.1, 661.7, 1004.7, and 2614.5 keV peaks. Microcalorimeter spectra were energy calibrated using a spline fit to the 32.2, 59.5, 72.8, 105.3, and 123.1 keV peaks. CZT spectra were found to require no additional energy calibration.

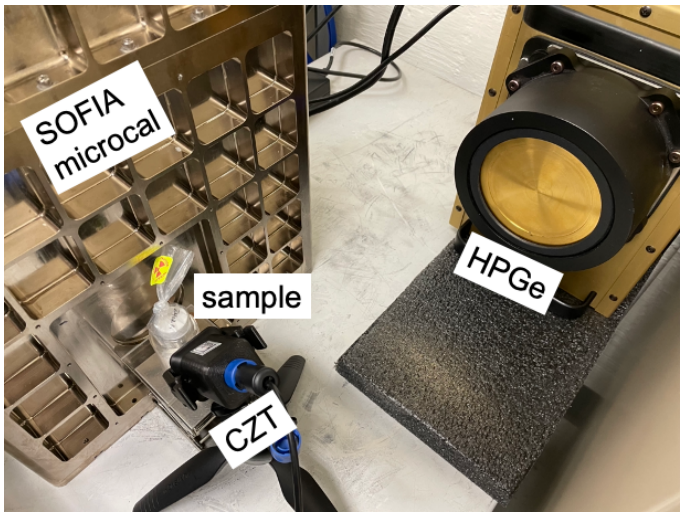

Figure 3: Configuration to allow simultaneous measurement of each sample with the three detector types. The relatively large high-purity germanium detector had to be placed back from the sample to limit its dead time.

Results

Figure 4 shows an overview of spectra from sample SR215A (46.9 GWd/MTU, discharged 2010) for each detector type. The IDM-200-P HPGe detector provided an energy range of 30 keV to 6 MeV, although identified peaks from the fuel samples were below 1.5 MeV. The CZT detector provided an energy range of 20 keV to 1.3 MeV with reasonable efficiency below 1 MeV. The microcalorimeter provided an energy range of 15-300 keV. The observed structure in the spectra highlights the complementary nature of HPGe (which provides high efficiency between 500-1500 keV with sufficient energy resolution to resolve most peaks in this region) and microcalorimetry (which can resolve the complex structure below 200 keV).

CZT spectra for each fuel sample are overlaid in Figure 5 with counts normalized to the 662 keV peak to simplify visual comparison. Identified peaks include Ba X-rays resulting from the decay of ^{134}Cs and ^{137}Cs, ^{241}Am, ^{154}Eu, ^{134}Cs, and ^{137}Cs. CZT provides moderate efficiency throughout the most important energy range but its energy resolution means that only major peaks can be resolved. In the case of on-line molten salt reactor safeguards, this limited information may be sufficient to confirm normal reactor operation at a high level, but the additional peaks resolved in HPGe and microcalorimeter spectra are much more sensitive to off-normal conditions.

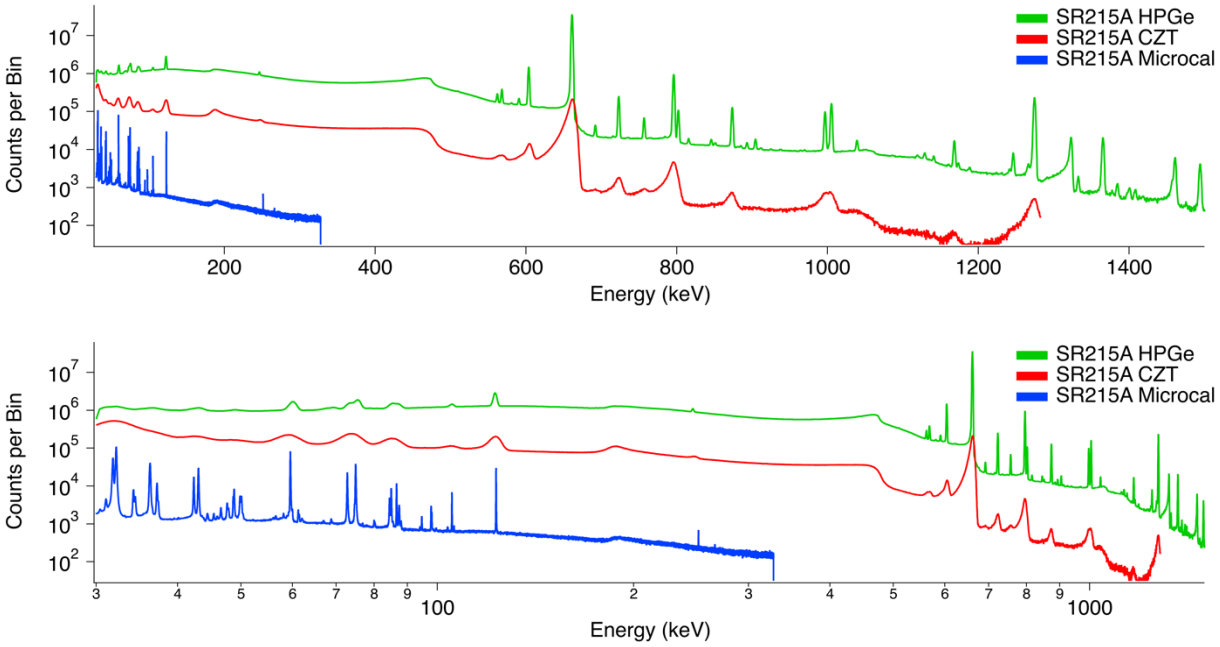

Figure 4: Comparison between spectra for CZT, HPGe, and microcalorimeter detectors illustrates the most useful energy range for each detector type. The top plot shows a linear energy scale and the bottom plot shows a logarithmic energy scale to better show peak structure in the low-energy region.

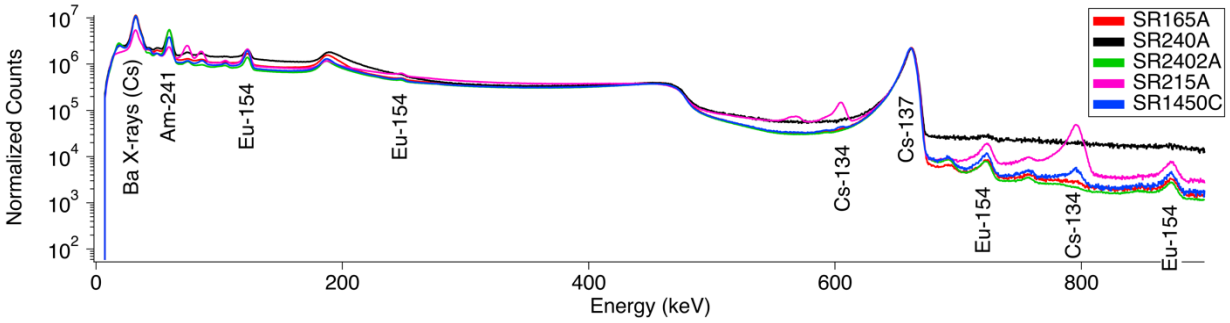

Figure 5: CZT spectra for all measured spent fuel samples. Spectra are normalized to the ^{137}Cs 662 keV peak amplitude.

IDM-200-P HPGe spectra are overlaid in Figure 6, again with counts normalized to the 662 keV peak. The HPGe spectra generally show the same identified nuclides as the CZT spectra, although with much better sensitivity. Additionally, there is a weak peak at 105.3 keV identified as ^{155}Eu (see Figure 10). ^{134}Cs is not clearly observed in CZT spectra of the older samples SR2402A, SR240A, and SR165A but multiple ^{134}Cs peaks are observed for all samples in the HPGe data. The ^{134}Cs/^{137}Cs ratio has been used as one of the best burnup indicators available with passive, nondestructive measurements [2]. ^{134}Cs is a "shielded" fission product that is mainly produced by neutron capture on other fission products, while ^{137}Cs is directly produced by fission with high yield. Figure 7 highlights the most intense ^{134}Cs and ^{137}Cs peaks observed in HPGe spectra. Their ratio clearly varies among the measured samples. Assuming a constant relative efficiency for each measurement, net counts in each of these peaks would be proportional to the ^{134}Cs/^{137}Cs ratio in the sample. Figure 8 shows the results of preliminary analysis using the Peakeasy software to fit the 605 and 796 keV peaks (net counts were combined to increase statistical precision) from ^{134}Cs and the 662 keV peak from ^{137}Cs. Due to the short half-life of ^{134}Cs (2.065 y) this peak ratio is very sensitive to cooling time soon after discharge, then becomes less sensitive and more difficult to measure as the ^{134}Cs decays. In order to use the ^{134}Cs/^{137}Cs peak ratio to determine burnup it is necessary to correct for cooling time which relies on knowledge of the fuel history. The "outlier" in the Figure 8 rightmost plot is sample SR215A which has a relatively recent discharge date of 2010.

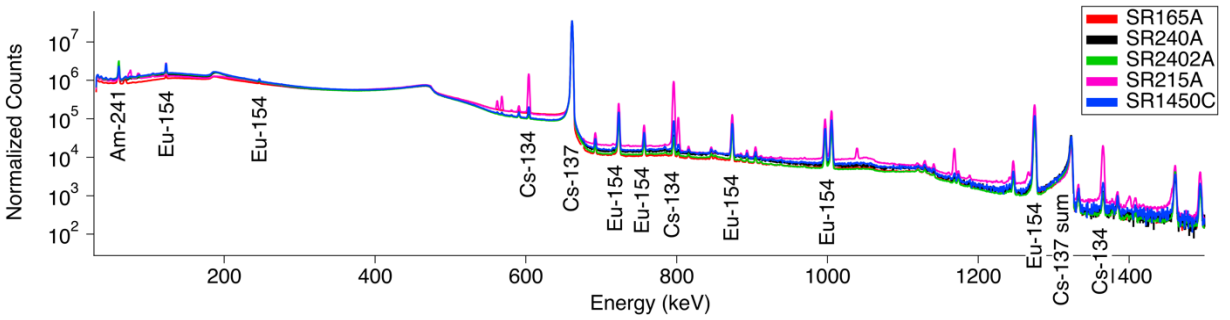

Figure 6: HPGe spectra for all measured spent fuel samples. Spectra are normalized to the ^{137}Cs 662 keV peak amplitude.

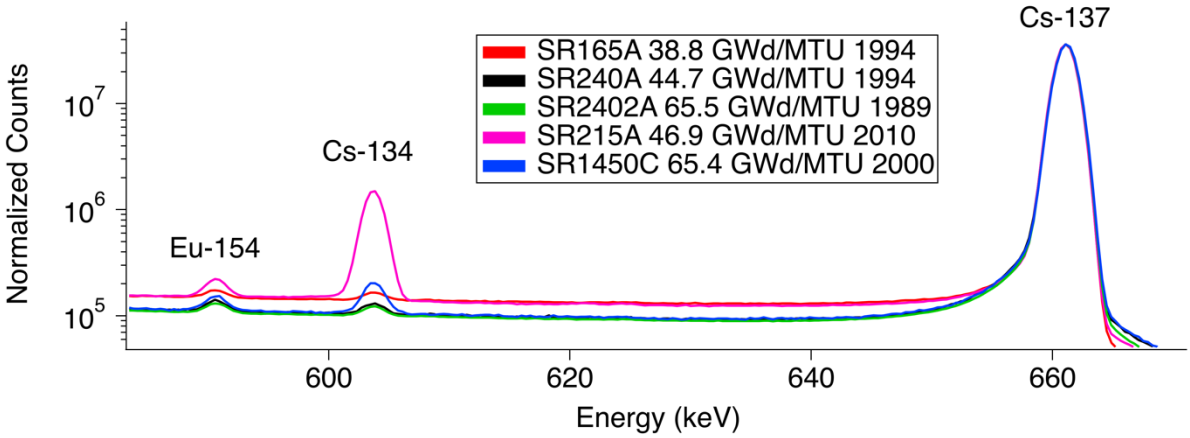

Figure 7: HPGe data in the 600 keV energy region. Spectra are normalized to the ^{137}Cs 662 keV peak amplitude to highlight variation in the ^{134}Cs/^{137}Cs ratio.

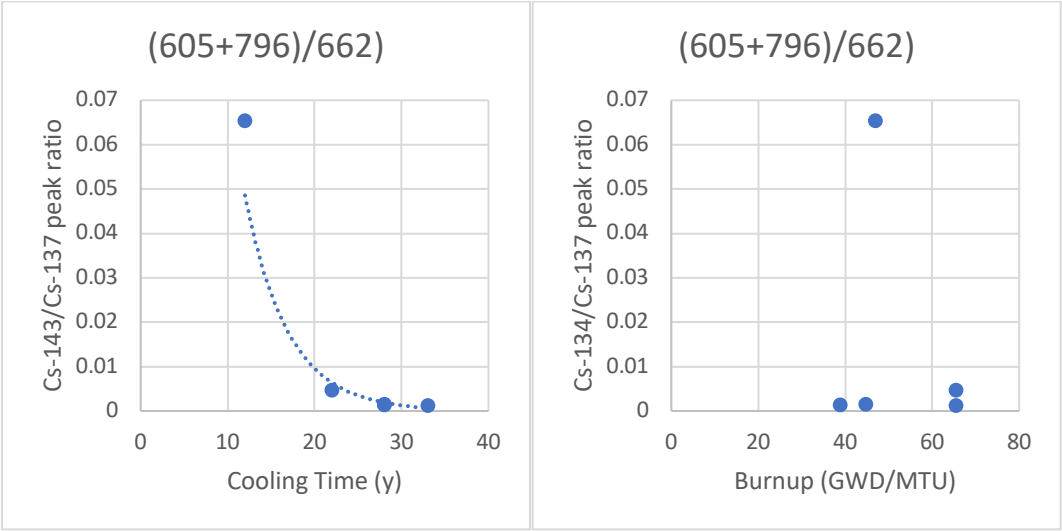

Figure 8: ^{134}Cs/^{137}Cs peak ratio calculated from net counts in both the 605 keV and 796 keV peaks relative to counts in the 662 keV peak, vs. cooling time and burnup.

Microcalorimeter spectra, normalized to the 123 keV peak, are overlaid in Figure 9. Gd X-rays from Eu decay, ^{243}Am, Pu X-rays from ^{239}Np decay, and ^{239}Np are identified in addition to ^{241}Am and ^{154}Eu that were observed in CZT and HPGe data. Figure 10 shows the 105 keV region where the 105.3 keV peak from ^{155}Eu is clearly observed along with two peaks resulting from the decay of ^{239}Np. The 74.7 keV direct gamma ray from ^{243}Am is also observed and was found to correlate well with the 103.7 and 106.1 keV peak intensities. As ^{239}Np (2.36 day half-life) quickly reaches equilibrium with its long-lived parent ^{243}Am, it can be used to accurately quantify the ^{243}Am.

Preliminary analysis using the Peakeasy software to fit peak ratios suggests that two additional ratios are available in the microcalorimeter data to determine burnup and cooling time (or periods of reactor shutdown). A constant relative efficiency curve was assumed for all measurements. The ^{239}Np(^{243}Am)/^{241}Am peak ratio is most sensitive to burnup and less sensitive

to cooling time as the ^{243}Am (7364 y half-life) and ^{241}Am (432.6 y half-life) are both long-lived actinides. Conversely, the ^{155}Eu/^{154}Eu ratio is very sensitive to cooling time as ^{155}Eu has a 4.75 y half-life and ^{154}Eu has a 8.60 y half-life. This ratio is also sensitive to burnup as ^{154}Eu is a "shielded" fission product that is primarily created through neutron capture on other fission products, while ^{155}Eu is directly produced by fission with a reasonably high yield. Compared to using only the traditional ^{134}Cs/^{137}Cs ratio to determine burnup, use of these two additional ratios have the potential to improve confidence in quantification of burnup and to reduce reliance on knowledge of fuel irradiation history.

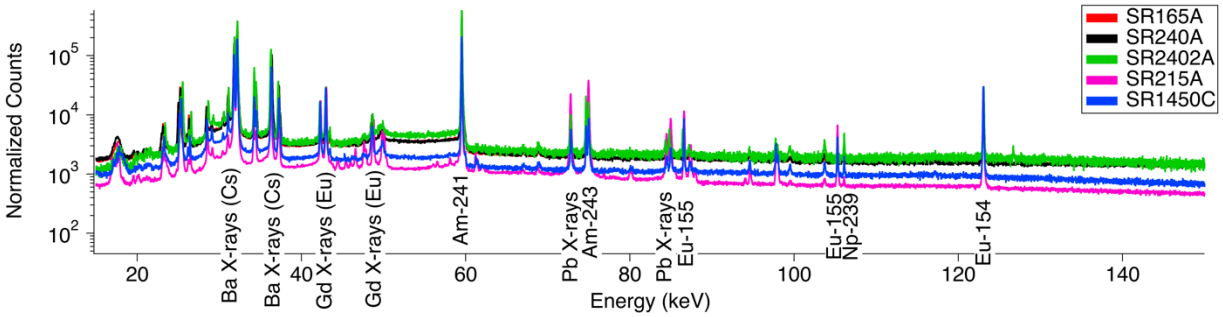

Figure 9: Microcalorimeter spectra for all measured spent fuel samples. Spectra are normalized to the ^{154}Eu 123 keV peak amplitude.

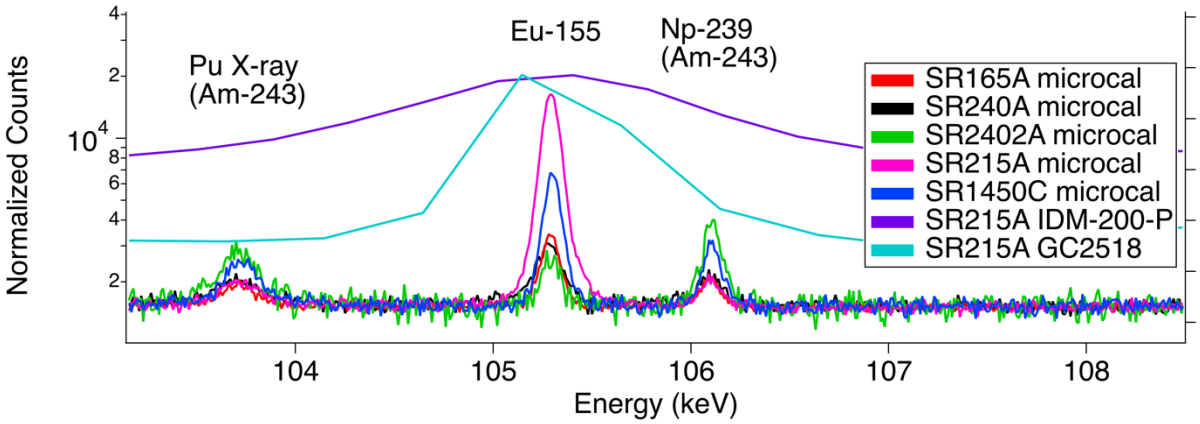

Figure 10: Microcalorimeter and HPGe (IDM-200-P and GC2518) data in the 105 keV energy region. Spectra are normalized to simplify visual comparison of peak ratios.

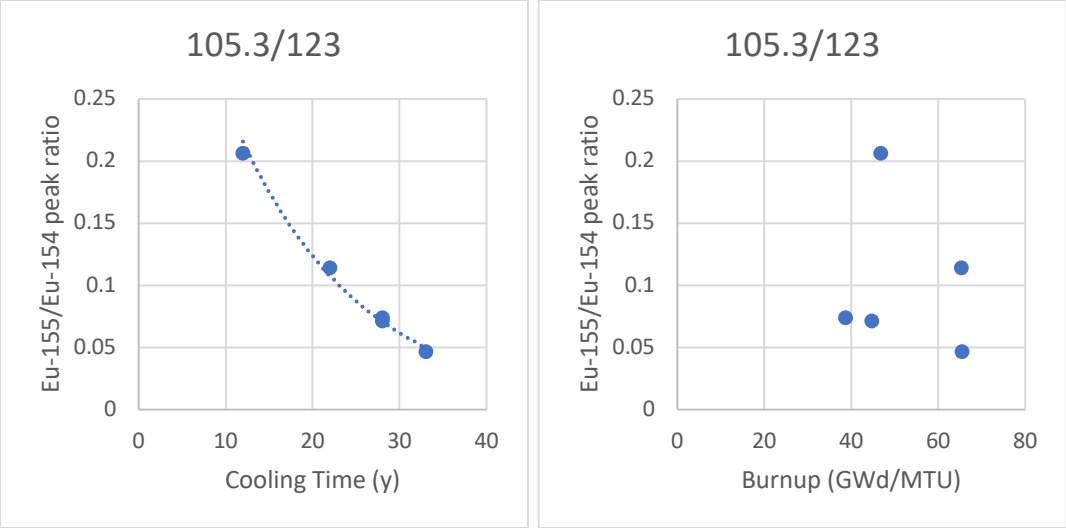

Figure 11: $^{155}Eu/^{154}Eu$ peak ratio calculated from net counts in the 105.3 keV peak relative to counts in the 123 keV peak, vs. cooling time and burnup. The $^{155}Eu/^{154}Eu$ peak ratio is very sensitive to cooling time but also sensitive to burnup if corrected for cooling time.

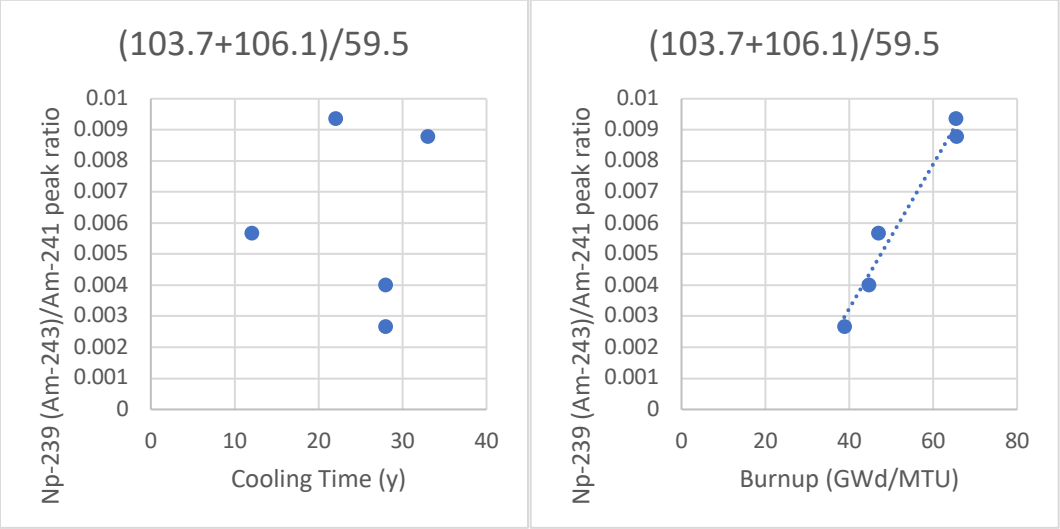

Figure 12: $^{239}Np/^{241}Am$ peak ratio calculated from net counts in both the 103.7 and 106.1 keV peaks relative to counts in the 59.5 keV peak, vs. cooling time and burnup. The $^{239}Np(^{243}Am)/^{241}Am$ peak ratio is most sensitive to burnup and less sensitive to cooling time.

Conclusions and Next Steps

This first measurement campaign employing traditional and advanced gamma spectroscopy technologies on dissolved irradiated fuel samples has demonstrated the potential to nondestructively determine important isotope ratios that correlate with fuel composition and irradiation history.

The main conclusions of this work are:

- Additional burnup and cooling time indicators are accessible in the low-energy part of the spectrum. $^{243}Am/^{241}Am$ is most sensitive to burnup and $^{155}Eu/^{154}Eu$ is sensitive to both cooling time and burnup. These ratios can provide more robust analysis of burnup and cooling time (or periods of reactor shutdown) compared to the traditional $^{134}Cs/^{137}Cs$ ratio which is sensitive to both and requires more information about reactor operation to interpret.
- High-purity germanium and microcalorimeter detectors are complementary in that they each provide the best available energy resolution in the high and low energy regions respectively.
- Cadmium zinc telluride detector resolution may be sufficient for limited characterization of fission product ratios to indicate burnup or normal reactor operation.

The gamma spectra of liquid fuel in an operating molten salt reactor will be dominated by additional short-lived fission products. However, it is likely that a combination of gamma spectroscopy technologies (especially HPGe and microcalorimetry together) will be useful in quantifying indicator fission product ratios for safeguards verification and detection of off-normal conditions.

Acknowledgement

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