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Development of Microcalorimeter Decay Energy Spectroscopy to Meet Safeguards Needs

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Microcalorimeter decay energy spectroscopy is a novel radiometric measurement technology under development for near-term use in safeguards analytical laboratories because of its potential to accurately determine the composition of small uranium, plutonium, and other actinide containing waste samples with 1 Bq or less of alpha activity, corresponding to 0.4 ng of Pu or 12 μg of U. These small sample quantities will simplify shipping procedures and minimize time between sample collection and analysis. As a radiometric technique complementary to mass spectrometry, decay energy spectroscopy can improve confidence in analytical results. Developing rapid sample preparation methods that yield high-resolution spectra is essential to achieving optimal measurement performance. We present results of ultrasonic welding as a new rapid sample preparation technique, giving an automated and more practical alternative to the currently-used manual mechanical alloying technique. High activity measurements will require the ability to deconvolve pulse pileup, particularly for high activity waste samples from spent nuclear fuel reprocessing that have high beta activity, and therefore challenge the analysis of the alpha isotopes. We will present quantitative analysis results of plutonium, uranium, and high activity waste samples, and highlight the potential of decay energy spectroscopy to aid analytical laboratories in meeting safeguards needs.

INTRODUCTION

Precise and accurate measurement of large numbers of U, Pu, and actinide containing waste samples is required each year in safeguards analytical laboratories. The conventional analysis approach is through a combination of alpha spectroscopy, mass spectrometry, and gamma spectroscopy. Altogether this procedure is highly time consuming, labor intensive, and requires complex chemical separations that generate significant radioactive waste.

Microcalorimeter Decay Energy Spectroscopy (DES) is a novel radiometric technique capable of reducing the time, labor, and cost associated with analyzing such samples. Using small radioactive samples with 1 Bq or less of alpha activity encapsulated in a microcalorimeter detector, DES can accurately determine composition by measuring the total decay energy for each alpha decaying nuclide with nearly 100% detection efficiency. This unique measurement gives ultra-high energy resolution (typical 0.8-2 keV FWHM at 5 MeV) with a much simpler spectrum than conventional alpha spectroscopy (Figure 1) [1]. DES can also serve as a second independent analytical method, complementary to mass spectrometry, in order to determine isotope ratios with high accuracy and increase confidence in the reported results.

This paper explores the use of DES as a practical analytical tool for analyzing small safeguards samples by presenting results from measured Pu, U, and mixed actinide samples, as well as isotopically impure samples such as trinitite and high activity waste sources. This paper will also demonstrate the importance of good sample preparation and its effects on DES spectra, including a discussion on future sample preparation technique development.

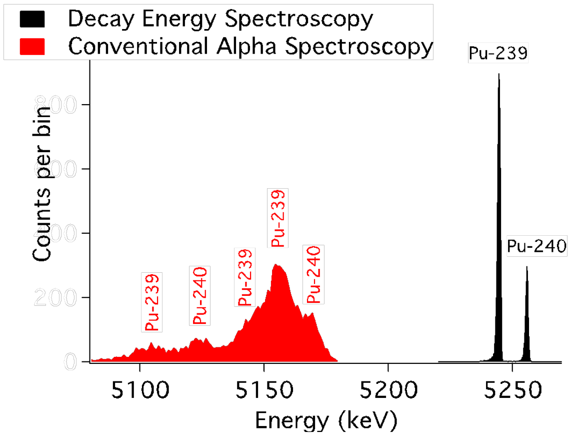

Figure 1. DES spectrum with easily resolved ^{239}Pu and ^{240}Pu peaks in contrast to the complex overlapping peaks in an alpha spectrum from a conventional silicon detector. DES measures the unique total nuclear decay energy for each alpha decaying nuclide using an ultra-high resolution microcalorimeter sensor, and eliminates the need for actinide chemical separations.

MEASUREMENT CAPABILITIES

Plutonium and Uranium

In order to evaluate DES capabilities, measurements were done on Pu and U certified reference materials (CRMs). Plutonium reference material results are shown in Figures 2 and 3. Uranium reference material results are shown in Figures 4 and 5. The acquisition time for all Pu and U spectra shown is 23 hours.

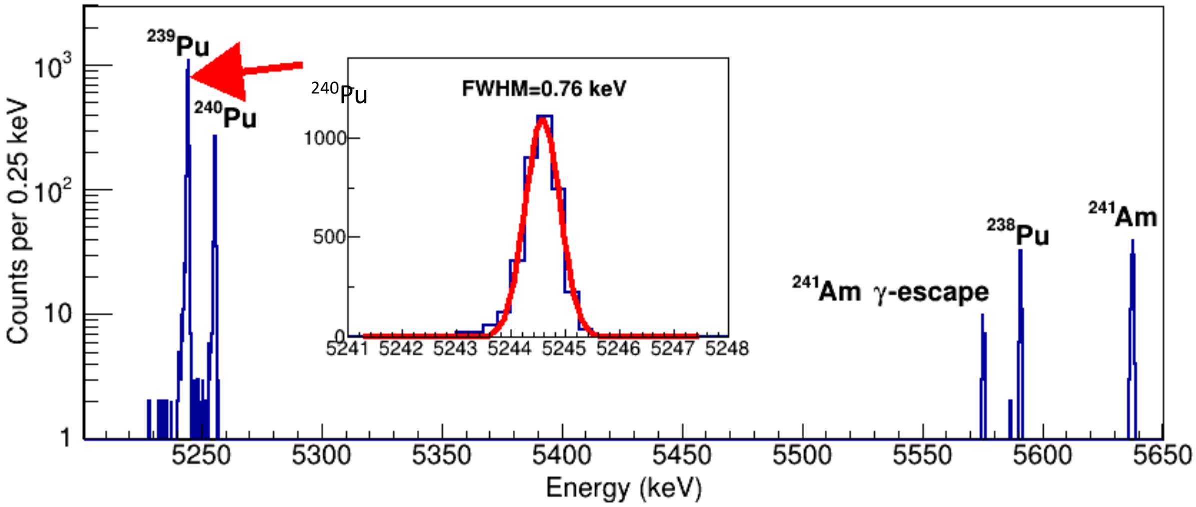

Figure 2. Decay energy spectrum of CRM126A (6% ^{240}Pu).

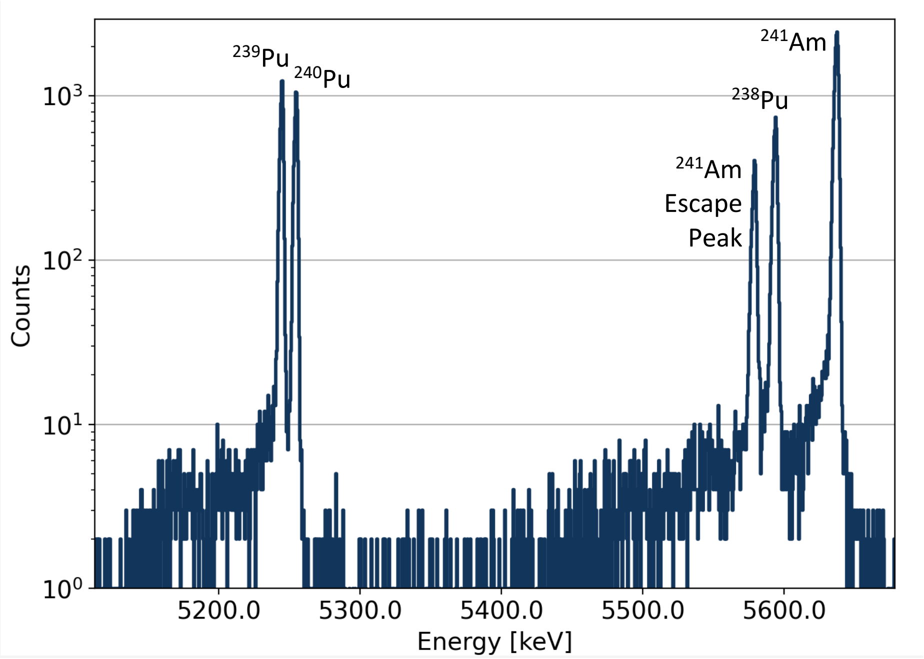

Figure 3. Decay energy spectrum of CRM137 (19% ^{240}Pu).

DES is able to clearly resolve ^{239}Pu, ^{240}Pu, ^{238}Pu, and ^{241}Am for both CRM126A and CRM137. The energy resolution of the decay energy spectrum of CRM126A is 0.76 keV FWHM at 5 MeV. The energy resolution of the decay energy spectrum of CRM137 is 2.5 keV FWHM at 5 MeV. Determined isotope ratios agree with declared values [2]. Overall, DES has shown precise and accurate measurements of very small plutonium samples, proving it is a useful tool in the analysis of small safeguards samples.

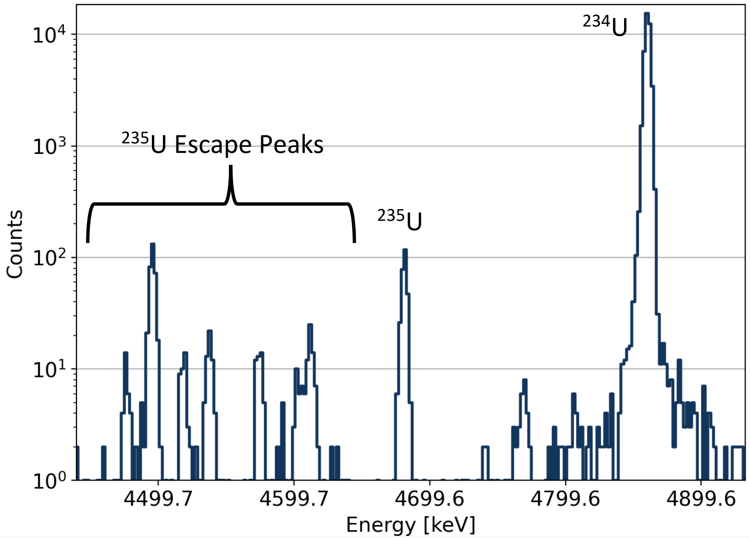

Figure 4. Decay energy spectrum of NBSU970 (97.7% ^{235}U).

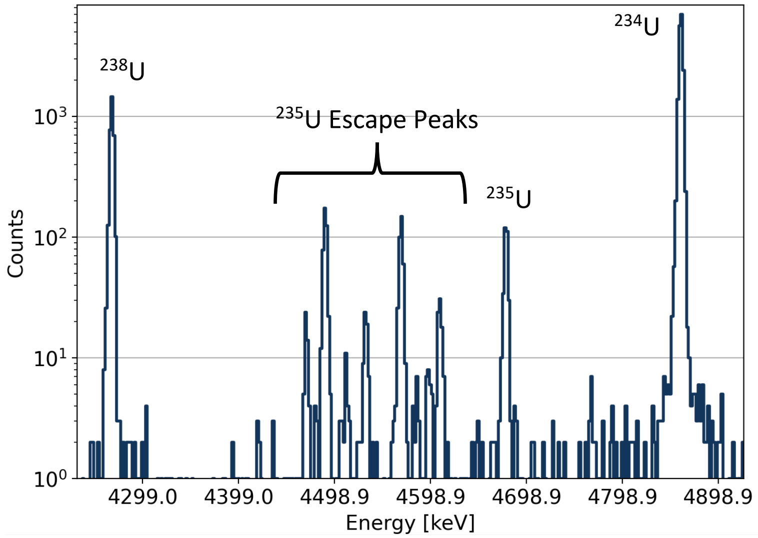

Figure 5. Decay energy spectrum of NBSU05 (5% ^{235}U).

For the highly-enriched uranium sample shown in Figure 4, the decay energy spectrum clearly resolves ^{234}U, ^{235}U, and ^{236}U. There were not enough counts collected for ^{238}U to clearly resolve the isotope. For the low-enriched uranium sample shown in Figure 6, the decay energy spectrum clearly resolves ^{234}U, ^{235}U, ^{236}U, and ^{238}U. For both of these uranium samples, the isotopic compositions determined by DES agree with the decay-corrected certified values [2].

Mixed Actinide Sample

To further evaluate DES capabilities, a mixed actinide sample solution with a known composition was measured. The resulting spectrum is shown in Figures 6 and 7.

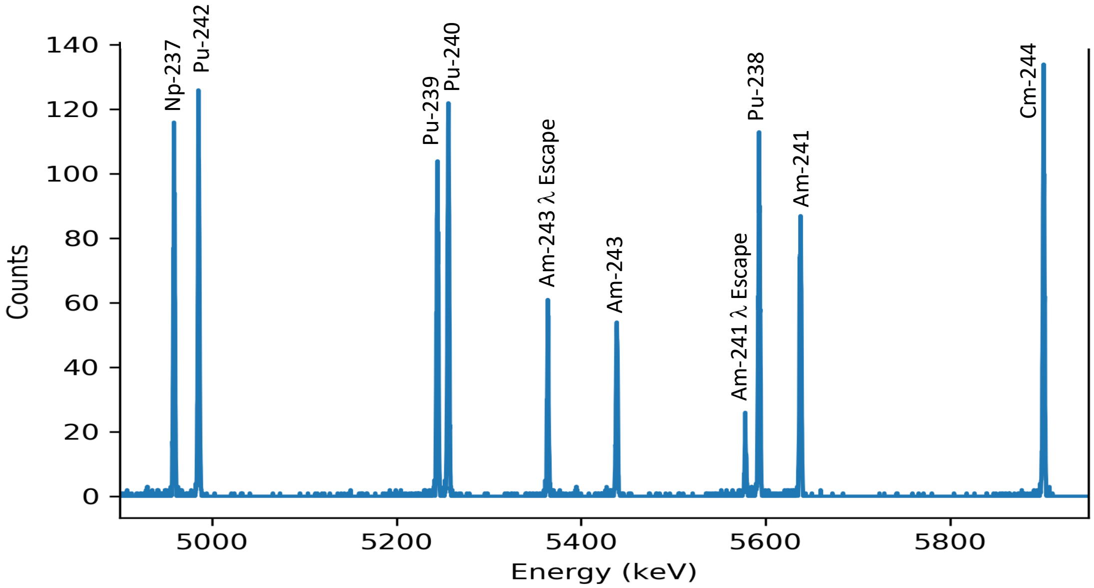

Figure 6. Decay energy spectrum of a mixed actinide sample solution.

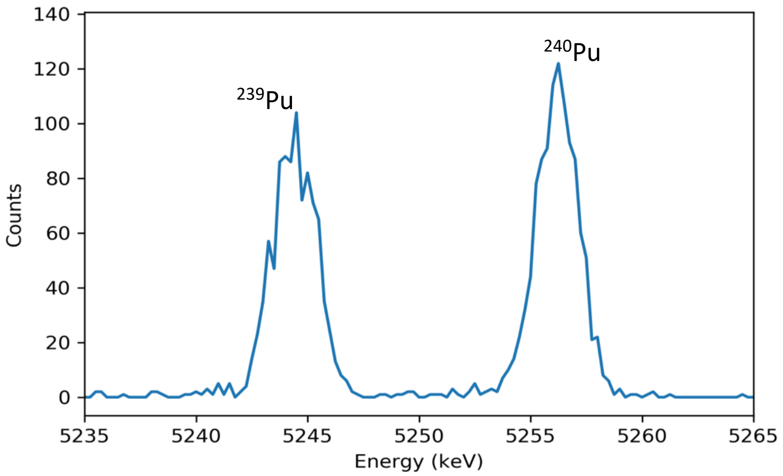

Figure 7. ^{239}Pu and ^{240}Pu region of the decay energy spectrum of the mixed actinide sample, zoomed in to highlight good peak shape, good energy resolution (2.1 keV FWHM), and minimal low-energy tailing.

The resulting spectrum shows resolved peaks for all alpha-decaying nuclides known to be present in the sample. The achieved energy resolution is 2.1 keV FWHM at 5 MeV, sufficient for isotopic analysis. DES is able to accurately quantify the composition of mixed actinide samples, further highlighting the potential of DES to aid analytical laboratories in meeting safeguards needs.

Impure Samples

In order to be a useful and practical tool for measuring real-world safeguards samples, DES needs to be able to accurately determine the composition of impure samples, meaning samples with unknown isotopes and significant non-radioactive impurities. An investigation was done using trinitite [3], where DES was able to accurately identify ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Am and obtain a decay-corrected ^{240}Pu/^{239}Pu mass ratio of 0.03 in a trinitite bead.

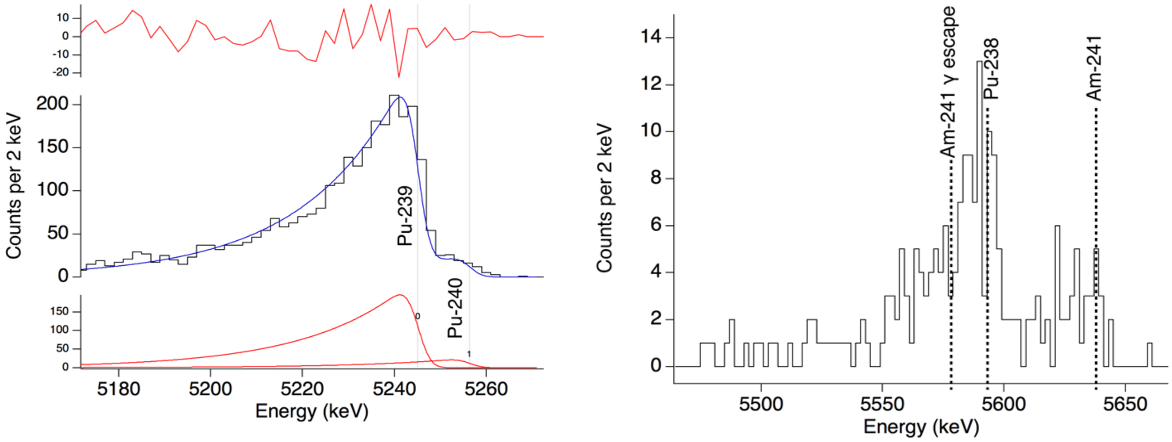

Figure 8. (Left) Peaks from ^{239}Pu and ^{240}Pu observed in trinitite. The middle plot shows the fitted spectrum, the top plot shows residuals, and the bottom plot shows the fit components. (Right) The presence of ^{238}Pu and ^{241}Am are also identified. Dashed lines indicate the expected peak locations. [3]

High Activity Waste Samples

High activity waste samples from spent nuclear fuel reprocessing have high beta activity, and therefore challenge the analysis of the alpha isotopes. Pulses from beta events complicate the analysis of the raw data due to a large number of pileup events; the standard analysis method of optimal filtering rejects pileup events. Longer acquisition times are needed to collect pulses free from pileup.

Other filtering methods can decrease the acquisition time by not rejecting pileup events. Here we show the results of using a bipolar cusp-like shaping (BCS) algorithm [4] to analyze data with moderate pileup due to beta decays (alpha:beta decay ratio of 1:15). The result is shown in Figure 9. The resolution when using this filter was 12 keV FWHM.

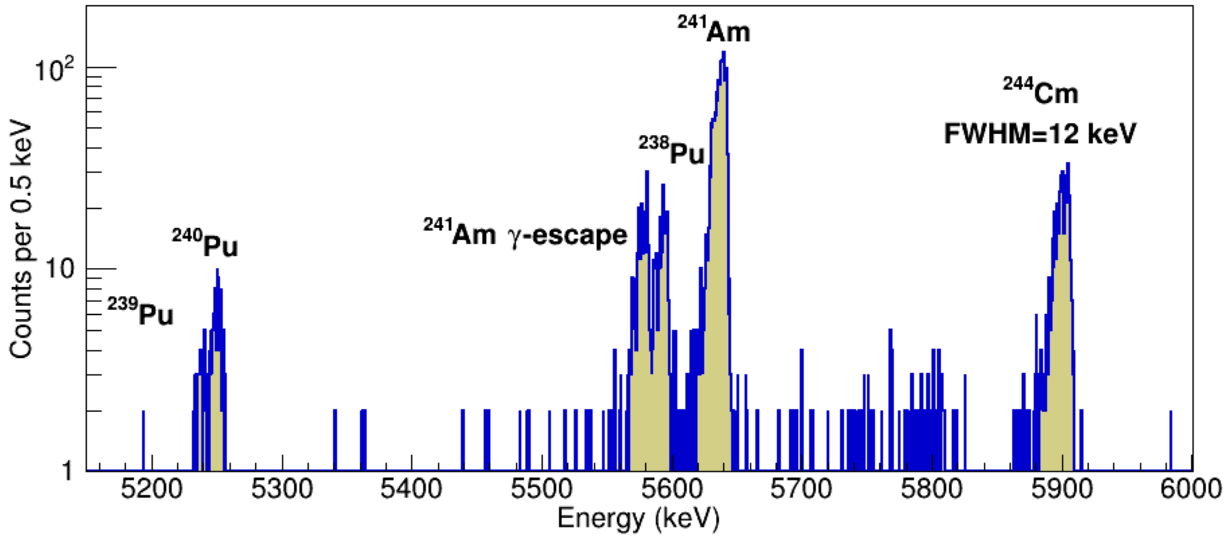

Figure 9. Result of the BCS filter applied to a sample with beta decays. No loss of resolution was observed compared to the optimal filter, and statistics were much higher.

SAMPLE PREPARATION

One element that makes DES an appealing safeguards measurement technique is the minimal and relatively simple sample preparation involved. Traditionally used techniques, such as alpha spectroscopy and mass spectrometry, require complex actinide chemical separations. DES, on the other hand, simply requires the sample particle to be incorporated in an absorber material with a low heat capacity. The technique for incorporating sample material in an absorber can vary, as well as the choice of absorber material [5]. It has been shown that a well-prepared DES sample has significant effects on the resulting spectra such as reduced low-energy tailing, reduced peak-splitting, and improved energy resolution [1]. Mechanically kneading a folded absorber with sample material inside has consistently yielded the best results. This process breaks up crystalline residue from sample solution and homogeneously distributes it throughout the absorber material to produce good energy thermalization [1]. The effects of this mechanical kneading process on the decay energy spectrum are shown in Figure 10. The effects of mechanical kneading on the cross-sectional grain structure of an absorber are shown in Figures 11 and 12. Grain structure is considered a proxy for the effectiveness of mechanical kneading.

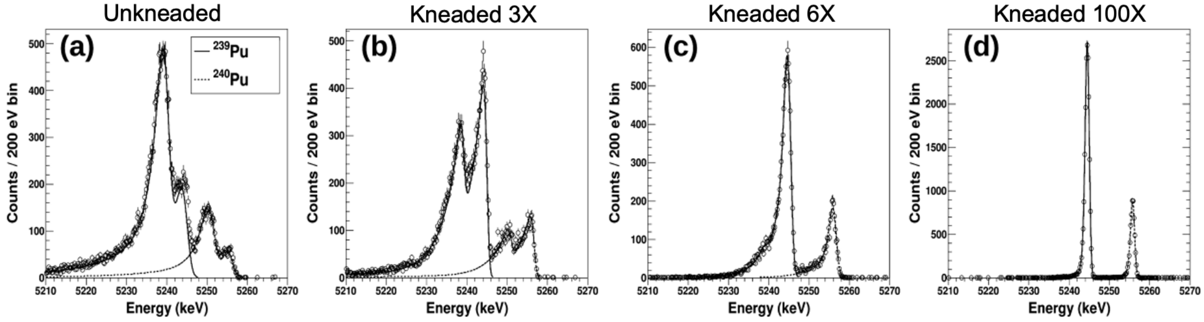

Figure 10. (From [1]) Measurement series showing the effects of mechanical kneading on an absorber with a ^{239}Pu/^{240}Pu sample. (a) Unkneaded absorber showing peak-splitting for each isotope. (b) Resulting spectrum after kneading the absorber three times, counts are starting to concentrate in the higher-energy peak for each isotope. (c) Resulting spectrum after kneading the absorber six times, no more peak splitting and an improved resolution. (d) Resulting spectrum after kneading the absorber 100 times. The final spectrum shows no peak splitting, minimal low-energy tailing, and a significantly improved resolution.

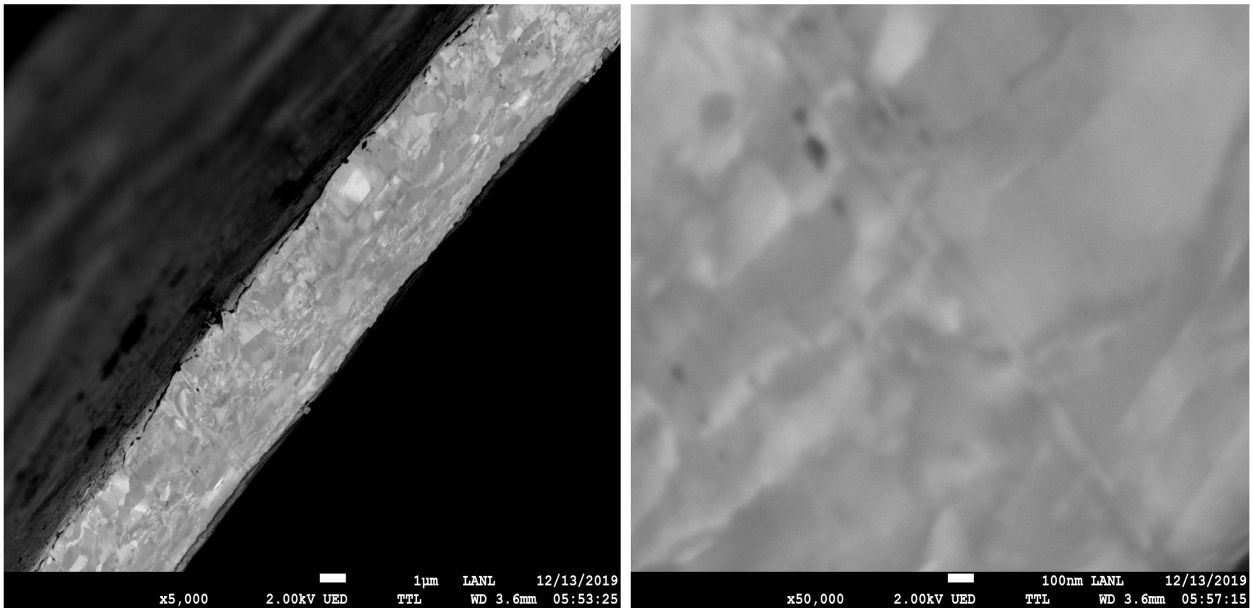

Figure 11. Cross section of an unkneaded gold foil absorber, shows wide grain size distribution with grains as large as 1 μm. Magnification is 5000x on left and 50000x on right.

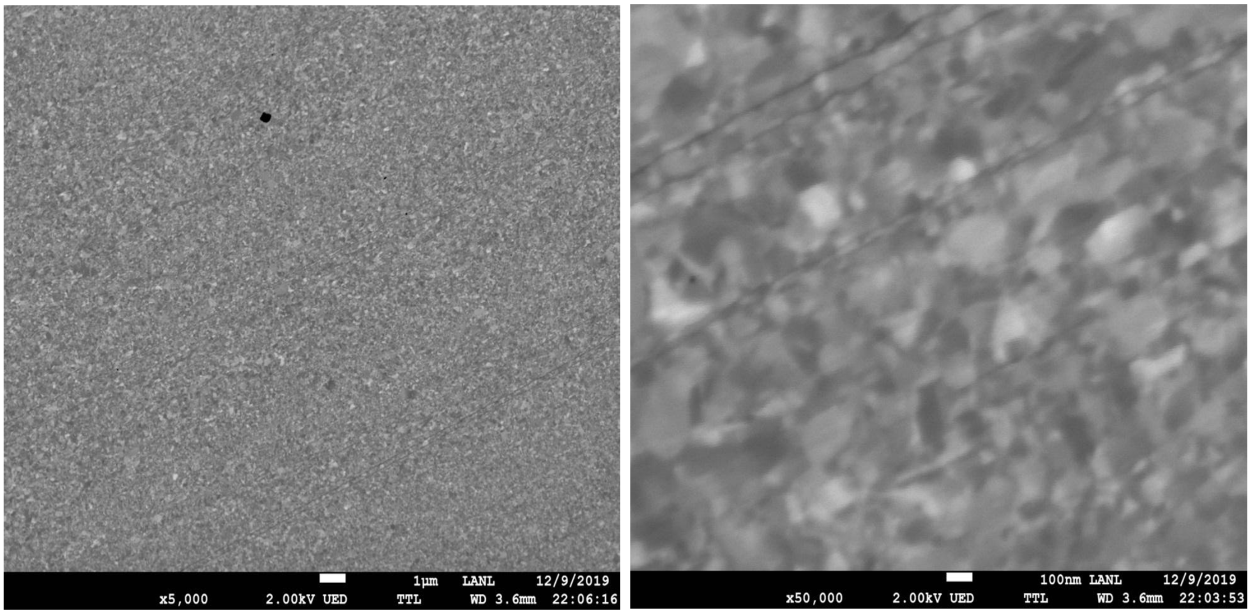

Figure 12. Cross section of a mechanically kneaded gold foil absorber, shows a more uniform grain structure with a smaller mean size. Magnification is 5000x on left and 50000x on right.

Though mechanical kneading has been proven to yield consistently good results (<1 keV FWHM at 5 MeV), the process is time consuming, tedious, and requires a degree of skill. In order for DES to be a more practical safeguards measurement technique, there is a strong need to automate the mechanical kneading process. Investigations have begun looking into ultrasonic welding and nanoporous absorber materials as alternatives to streamlining the mechanical kneading process.

In industry, ultrasonic welding is capable of fracturing oxide layers that occur on metal surfaces and incorporating those fractured oxides into the weld zone. This process shows great potential for incorporating nuclear material samples into a metal matrix to produce a structure similar to a mechanically kneaded absorber. Initial welding tests using non-radioactive material have shown good distribution of material throughout the matrix. Figure 13 below shows the cross section of a piece of gold foil ultrasonically welded between two pieces of tin. The result shows one seamless piece of tin with tiny pieces of gold spread throughout the tin cross section. This suggests ultrasonic welding has the potential to disperse radioactive material across a metal matrix as well. Current investigations are focused on ensuring no cross-contamination will occur between welded radioactive samples, and no airborne contamination will occur while welding radioactive material. Once a safe welding procedure is established, we will be able to prepare ultrasonically welded radioactive samples to measure using DES.

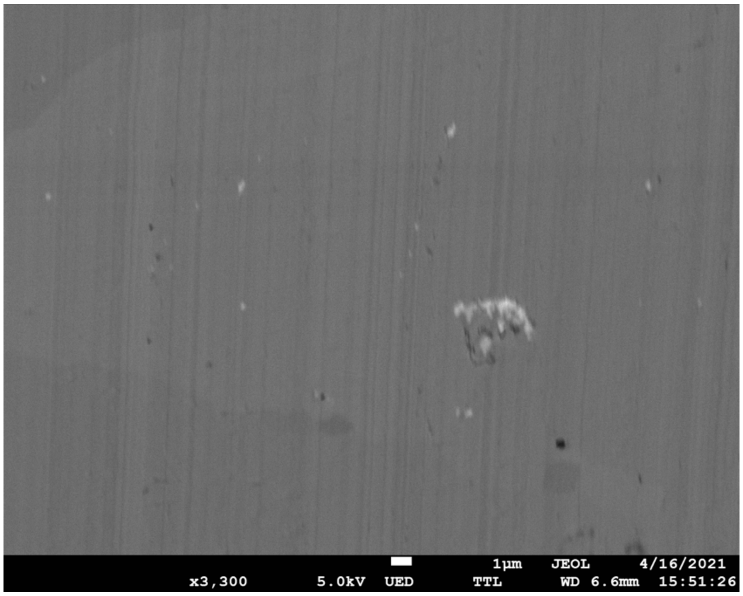

Figure 13. SEM image of the cross section of gold foil ultrasonically welded between two pieces of tin. The lighter colored specks in this image were identified as gold and were spread throughout the tin matrix.

The use of nanoporous materials as absorbers for DES could allow sample preparation to be as simple as pipetting sample solution onto a piece of pre-prepared nanoporous material and allowing it to dry. The result would be a nanocomposite structure similar to a mechanically kneaded absorber that could be attached to a microcalorimeter sensor and measured. Initial evaluation into this technique was done using a gold nanofoam made by removing silver from a gold-silver alloy using nitric acid. The resulting spectrum minimized peak splitting, but suffered from significant low-energy tailing. This tailing is likely attributed to a poor distribution of pore sizes, and we expect to see improvements as the mean pore size is reduced.

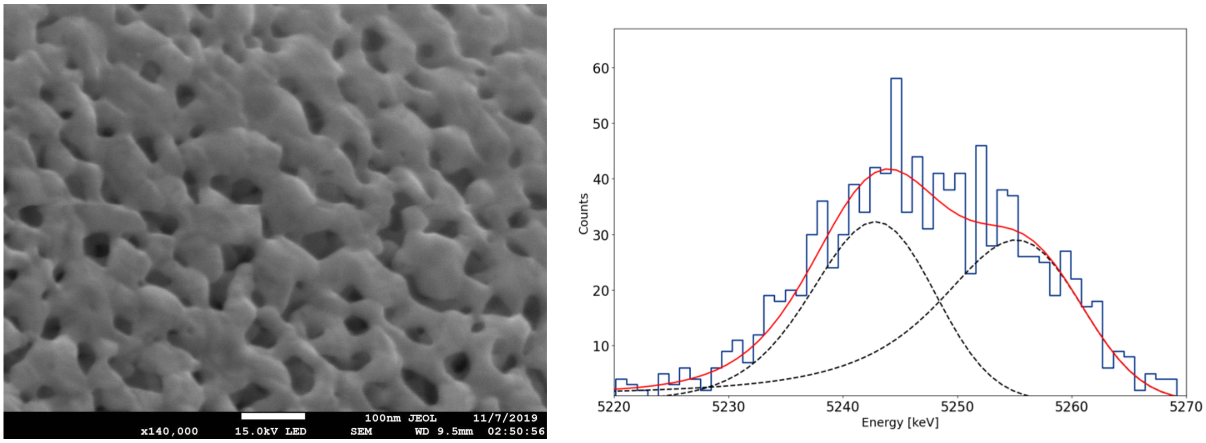

Figure 14. (Left) SEM image of gold nanofoam made by removing silver from a gold-silver alloy using nitric acid. (Right) Decay energy spectrum of CRM137 dried in gold nanofoam. This plot shows the ^{239}Pu/^{240}Pu region. The two peaks are distinguishable, but the low-energy tailing and poor energy resolution make it a challenging quantification.

CONCLUSIONS

We have demonstrated the importance of microcalorimeter decay energy spectroscopy as a useful and practical measurement technique to aid safeguards laboratories. DES has successfully measured and quantified small (1 Bq or less of alpha activity) plutonium and uranium certified reference materials, mixed actinide samples, and high-activity waste samples from spent nuclear fuel. We have also demonstrated the importance of sample preparation for DES, and we have shown the need to automate the established mechanical kneading sample preparation technique. Initial investigations into ultrasonic welding and the use of nanoporous absorber materials show promising results that motivate the continued development of these techniques in order to make DES a more efficient measurement tool. Overall, DES has the potential to improve safeguards analytical laboratory's capabilities and efficiency by simplifying sample shipment procedures, reducing sample preparation and need for chemical separations, reducing time between sample collection and analysis, and minimizing hazardous waste.

ACKNOWLEDGEMENTS

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