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DESTRUCTIVE VERSUS NONDESTRUCTIVE ASSAY COMPARISONS USING THE SWEPP GAMMA-RAY SPECTROMETER

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ABSTRACT

In support of data quality objectives for the INEEL Stored Waste Examination Pilot Plant (SWEPP) a series of 208-liter (55-gallon) waste drums containing inorganic sludge have been sampled and destructively analyzed. The drums were non-destructively assayed by the SWEPP PAN system and the SWEPP Gamma-Ray Spectrometer (SGRS) prior to sampling. This paper reports some of the conclusions from the destructive versus NDA comparisons, and additionally presents the results of an on-going effort to use the destructive analyses to validate absolute efficiency curves calculated using Monte-Carlo and analytical modeling for the SGRS.

Destructive analysis results are available from radiochemical assay of 128 sludge-containing drums. The content codes represented are CC001 (42 items), CC002 (8), CC007 (48), CC800 (16), CC803 (3), and CC807 (11.) Each drum had two full-length vertical cores removed from designated radial positions. The entire length of each core was composited and submitted for analysis. All of the core composites were analyzed radiochemically for Am-241, Pu-239/240, and Pu-238, and by inductively-coupled mass spectrometry (ICPMS) for U-235 and U-238.

Not only have the destructive analysis results been useful in documenting the performance of both the SGRS and the PAN system, but also have allowed the determination of certain absolute counting efficiency values for the SGRS. The values, in turn will allow us to validate SGRS counting efficiencies computed by MCNP and analytical modeling, and perhaps use the SGRS as an absolute assay technique.

1.0 INTRODUCTION

Comparative measurement results for sludge drums were obtained from destructive radioassay of core samples from randomly selected drums that had been previously assayed using the NDA instruments at the Stored Waste Examination Pilot Plant (SWEPP). The Argonne National Laboratory-West (ANL-W) facility at the INEL was used for coring and sampling of inorganic sludge waste drums. Originally motivated for sampling of Resource Conservation Recovery Act (RCRA) listed hazardous constituents,

core sampling plans were modified to include radioassay analysis as well. These measurements were initiated primarily to aid in determination of the sludge drum assay bias of our Passive Active Neutron (PAN) system. The results of this work are reported in an accompanying paper at this conference.[1] However, the destructive analysis data have also been used to investigate the performance of the SWEPP Gamma-Ray Spectrometer (SGRS) for determination of radioisotopic mass ratios, and to determine the feasibility of using the SGRS as a quantitative assay technique for sludge-containing drums.

2.0 DESTRUCTIVE SAMPLING AND ANALYSES

Two 5-cm diameter core samples were removed from each drum by drilling from top to bottom at a radial location specified by the sampling plan. The radial core drill position was chosen at random from the selection of seven possible locations shown in Figure 1. Each core sample was blended to produce a composite sample representative of the total removed core. Samples of this composite were then removed and submitted for radiochemical analysis. Additional samples from the composite were reserved for RCRA analyses.

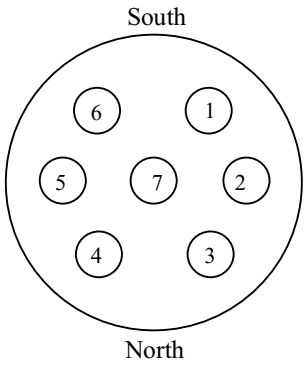

Figure 1 Radial positions for core drilling

Samples from each composite were dissolved and analyzed for ^{238}Pu, $^{239+240}Pu$, and ^{241}Am by valence adjustment, ion exchange separation of Am and Pu, and alpha spectrometric analysis. Attempts to quantify the Uranium isotopes by this technique produced results with unacceptably high uncertainties because of the low specific activities of these nuclides. Consequently, ^{235}U and ^{238}U were analyzed using inductively coupled plasma mass spectrometry (ICPMS.) Radioassay results for Pu and Am were produced for all 128 sludge drums sampled. Logistics limited the number of ICPMS uranium analyses to 56 drums, and analytical problems (discussed later) limited the number of fully useful results to 17.

Analytical results from each composite sample (two per drum) and replicate analyses performed on certain samples were averaged to provide a best estimate result of a drum's content. Weighted averaging was used. Each value was weighted by the reciprocal of its uncertainty squared.

3.0 SGRS MASS RATIO COMPARISONS

3.1 Methodology

The SWEPP Gamma-Ray Spectrometer (SGRS) uses INEEL-developed software[2] to measure the isotopic ratios of radioactive species in 55-gallon waste drums assayed at SWEPP. The system is used to confirm a weapon's grade (WG) isotopic distribution for the Pu within a drum, to determine the $^{241}Am/^{239}Pu$ for total alpha content, and the $^{235}U/^{239}Pu$ ratio for correction of the active PAN results for U content.

The importance of these isotopic ratio measurements to the characterization of sludge-containing waste drums stored at SWEPP is evident from the data in Figures 2 and 3. Figure 2 shows the distribution of the SGRS-measured $^{235}U/^{239}Pu$ mass ratios for 1290 sludge-containing waste drums at SWEPP, while Figure 3 gives a similar breakdown for the $^{241}Am/^{239}Pu$ mass ratio in 1303 drums. When ^{235}U is a significant fraction of the total fissile content in a drum, corrections must be made to the active PAN assay result in order to determine the correct TRU content. When the $^{241}Am/^{239}Pu$ mass ratio is greater than or equal to 0.5, the ^{241}Am activity is ≥ 98% of the total alpha content.

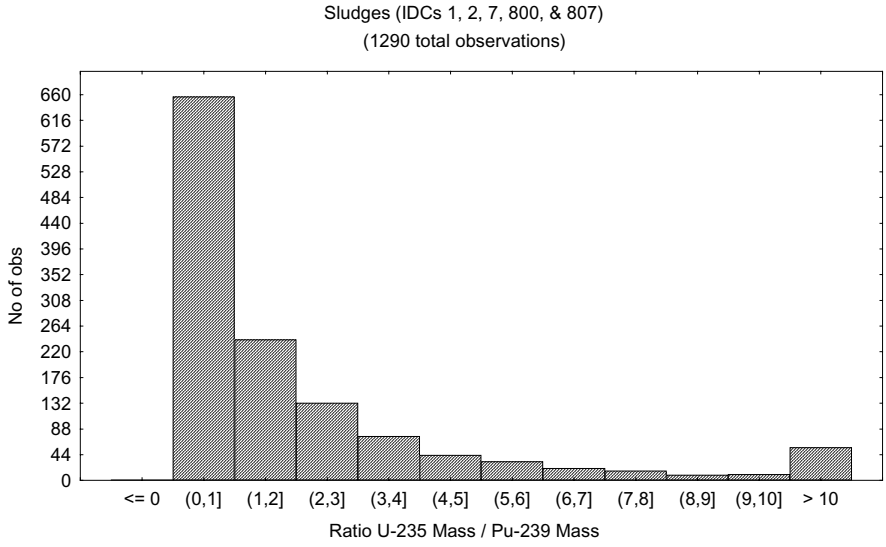

Figure 2 Sludge drum results sorted by $^{235}U/^{239}Pu$ mass ratio

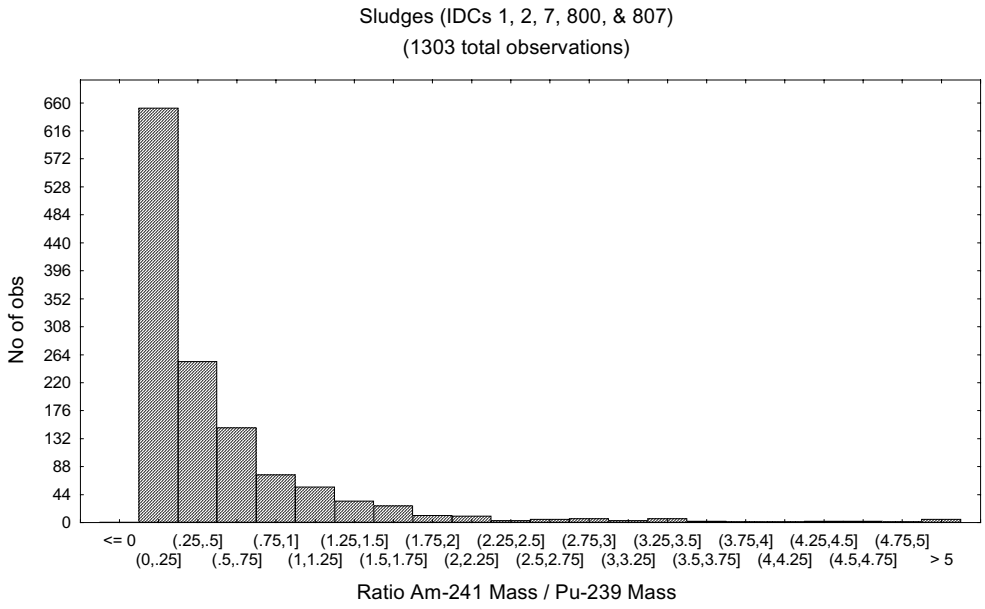

Figure 3 Sludge drum results sorted by $^{241}Am/^{239}Pu$ mass ratio

The SGRS system has been cross-checked on a small number of sludge-containing waste drums versus the popular MGA[3] and FRAM.[4] Results were compared for measured ratios of $^{238}Pu/^{239}Pu$, $^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$, $^{241}Am/^{239}Pu$, and $^{235}U/^{239}Pu$. The agreement between techniques was excellent.[5]

The destructive analysis results were adjusted for the contribution of ^{240}Pu to the $^{239+240}Pu$ concentrations assuming WG Pu isotopics. Each analytical activity result was converted to a mass value using the relevant specific activity and the mass values ratioed to compute the desired mass ratios. The ratio uncertainty was estimated by propagating the relative standard deviation of each analytical result in quadrature. Individual assay uncertainties were not specified for the ICPMS uranium results. From conversations with the analysts these results were assigned relative uncertainties of ±20% (1σ) for ^{235}U and ±5% (1σ) for ^{238}U.

Spectra acquired with the SGRS prior to drum coring were analyzed with the latest version of the SGRS code (Version 5.) The SGRS generated NDA result for each mass ratio was compared with the mass ratio computed from the destructive analyses. If replicate SGRS measurements were performed on a given drum, each replicate was used in the comparisons.

To facilitate the comparisons, a value computed by dividing the SGRS mass ratio by the destructive analysis mass ratio expressed as a percentage was termed the "% recovery." The relative standard

deviation on each % recovery value was computed by simple quadratic propagation of the individual relative standard deviations.

3.2 Data and Results

Am-241/Pu-239 Mass Ratio

Summary statistics for the % recovery of the radiochemical value for the $^{241}Am/^{239}Pu$ mass ratio by the SGRS NDA measurement are presented in Table 1. Two columns are presented. The first details the results for all the available data, while the second shows the results with selected outliers removed from the data set. No rigorous test was used to define outliers. Generally values less than 10% recovery and greater than 300% recovery were removed. A frequency histogram of the % recovery values is given as Figure 4 while a comparison plot of the destructive versus nondestructive results is given in Figure 5.

Table 1 Summary statistics for % recovery of the measured $^{241}Am/^{239}Pu$ mass ratio

	All values	*Eliminate 1 low and 2 high flyers*
Mean	102.66	100.17
Standard Error	3.99	3.33
Median	91.19	91.14
Mode	#N/A	#N/A
Standard Deviation	46.65	38.55
Sample Variance	2176.30	1485.96
Kurtosis	8.23	7.62
Skewness	2.52	2.33
Range	312.54	258.49
Minimum	13.55	33.83
Maximum	326.09	292.33
Sum	14064.67	13423.24
Count	137.00	134.00

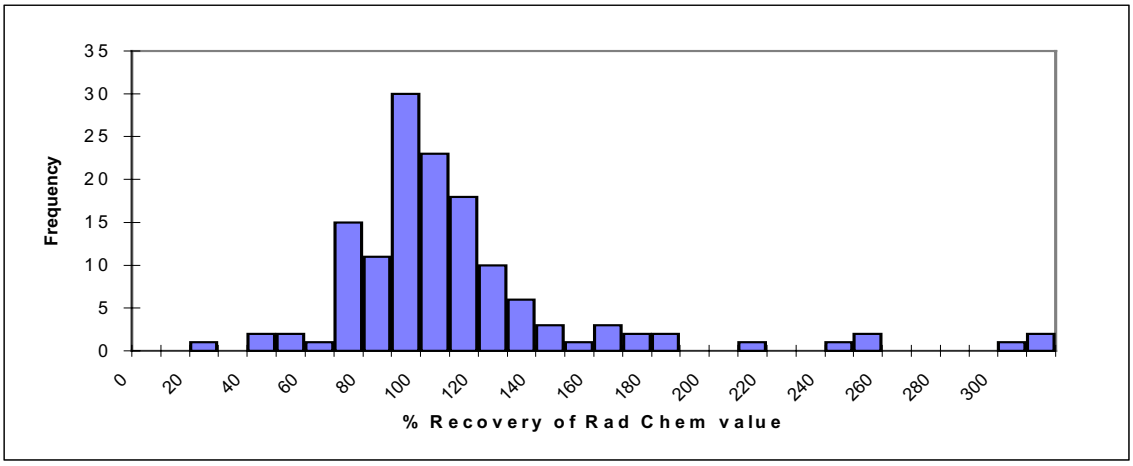

Figure 4 Frequency histogram for % recovery of the measured $^{241}Am/^{239}Pu$ mass ratios (all values)

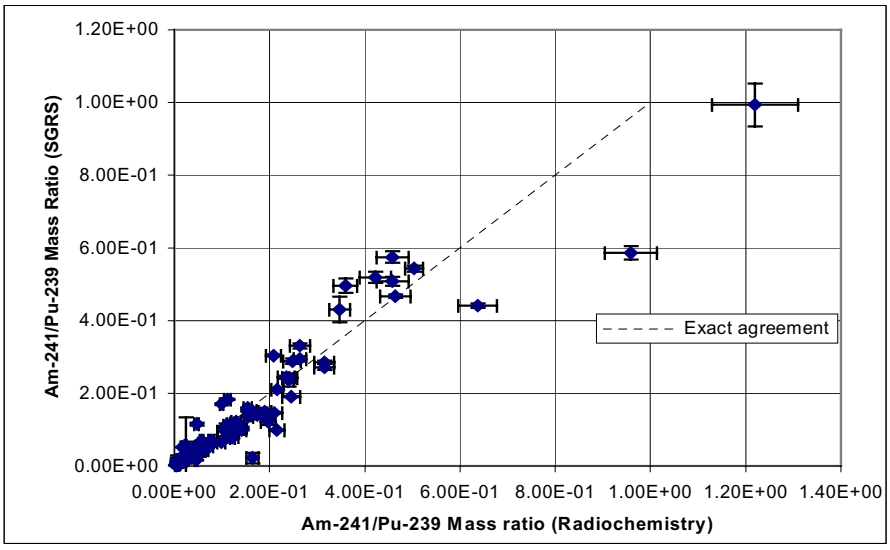

Figure 5 Comparison of destructive (radiochemistry) versus NDA (SGRS) values for the $^{241}Am/^{239}Pu$ mass ratio

U-235/Pu-239 Mass Ratio

Summary statistics are presented in Table 2. Figure 6 presents the frequency histogram while the destructive and nondestructive results are compared in Figure 7. The ICPMS uranium analyses were plagued by reagent blanks that from time to time exceeded the sample result determined just before or after the blank assay. The results were not blank corrected; however, each analysis that had a potential high blank problem was identified (flagged) on the analysis report. Consequently, a set of uranium analysis results that had no flagged analytical problems was selected and these results tracked.

Table 2 Summary statistics for % recovery of the measured $^{235}U/^{239}Pu$ mass ratio

	All values	*Eliminate 2 low and 4 high flyers*	*No Analytical Flags*
Mean	2.78E+02	9.44E+01	7.42E+01
Standard Error	1.55E+02	5.17E+00	7.07E+00
Median	8.81E+01	8.66E+01	8.00E+01
Mode	#N/A	#N/A	2.84E+01
Standard Deviation	1.22E+03	3.87E+01	2.91E+01
Sample Variance	1.48E+06	1.50E+03	8.49E+02
Kurtosis	5.91E+01	2.53E+00	1.44E+00
Skewness	7.62E+00	1.20E+00	2.19E-01
Range	9.59E+03	2.07E+02	1.19E+02
Minimum	5.78E+00	2.71E+01	2.71E+01
Maximum	9.60E+03	2.34E+02	1.46E+02
Sum	1.72E+04	5.29E+03	1.26E+03
Count	6.20E+01	5.60E+01	1.70E+01

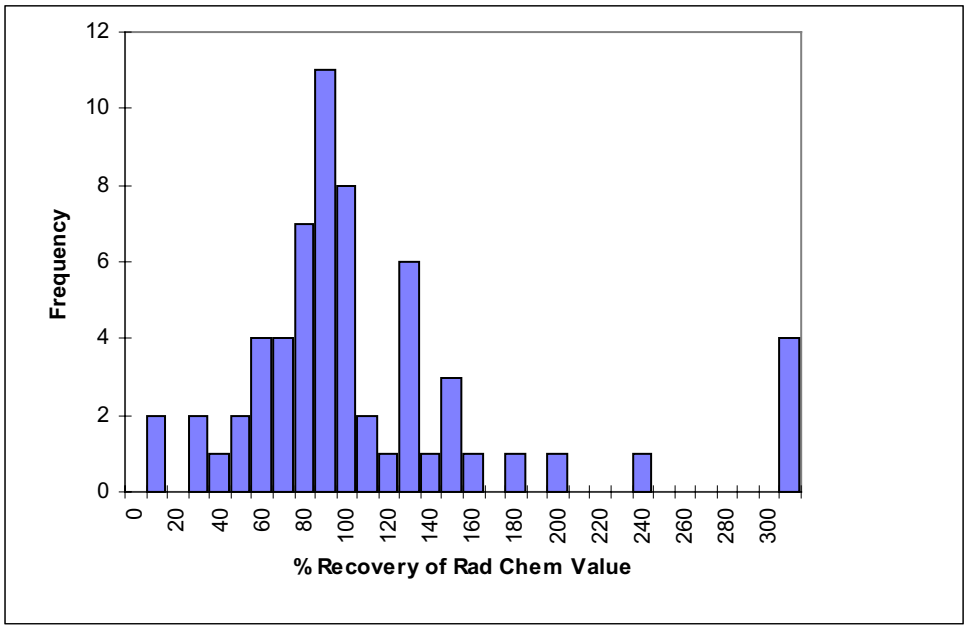

Figure 6 Frequency distribution for % recovery of the measured $^{235}U/^{239}Pu$ mass ratio (all values)

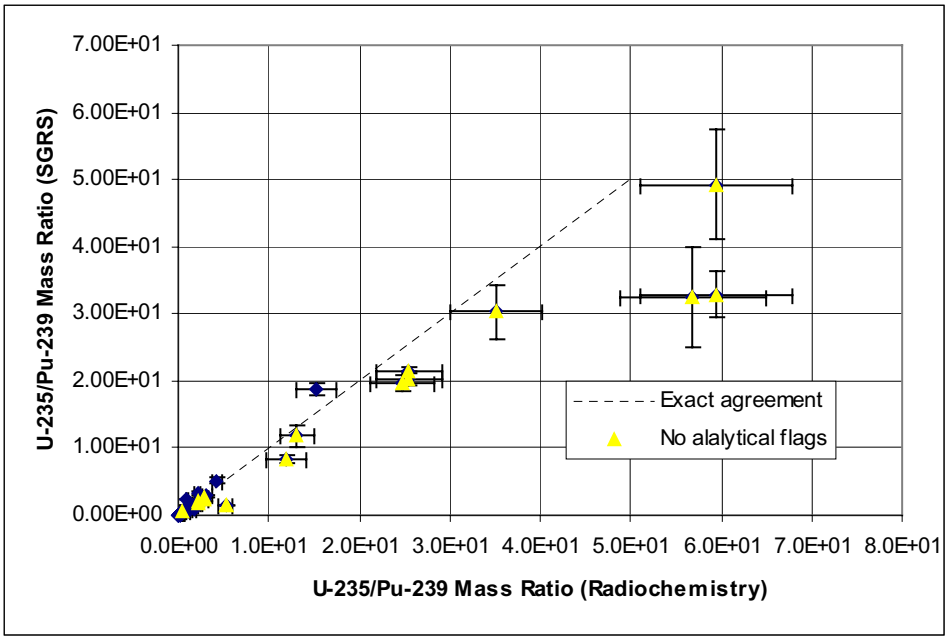

Figure 7 Comparison of destructive (Radiochemistry) versus NDA (SGRS) values for the $^{235}U/^{239}Pu$ mass ratio. Four values with % recoveries > 300% and 2 values with % recoveries < 10% are not plotted.

238-Pu/239-Pu Mass Ratios

Summary statistics are presented in Table 3 (for all values.) Figure 8 presents the frequency histogram while the destructive and nondestructive results are compared in Figure 9.

Table 3 Summary statistics for the $^{238}Pu/^{239}Pu$ mass ratio % recovery

	All Values
Mean	1.43E+03
Standard Error	2.42E+02
Median	3.02E+02
Mode	#N/A
Standard Deviation	2.69E+03
Sample Variance	7.22E+06
Kurtosis	3.38E+01
Skewness	4.78E+00
Range	2.30E+04
Minimum	7.92E-02
Maximum	2.30E+04
Sum	1.76E+05
Count	1.23E+02

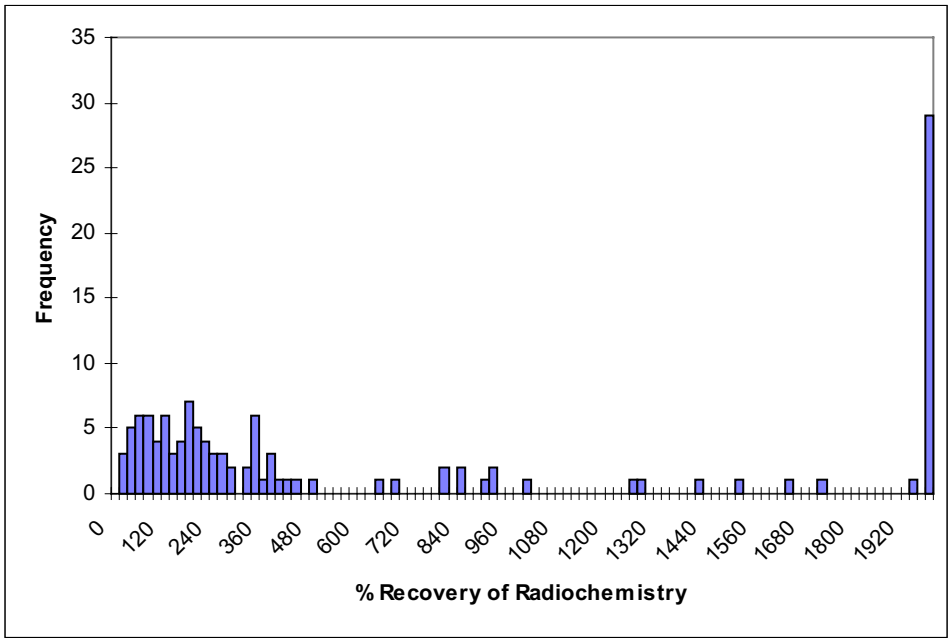

Figure 8 Frequency distribution for % recovery of the measured $^{238}Pu/^{239}Pu$ mass ratio

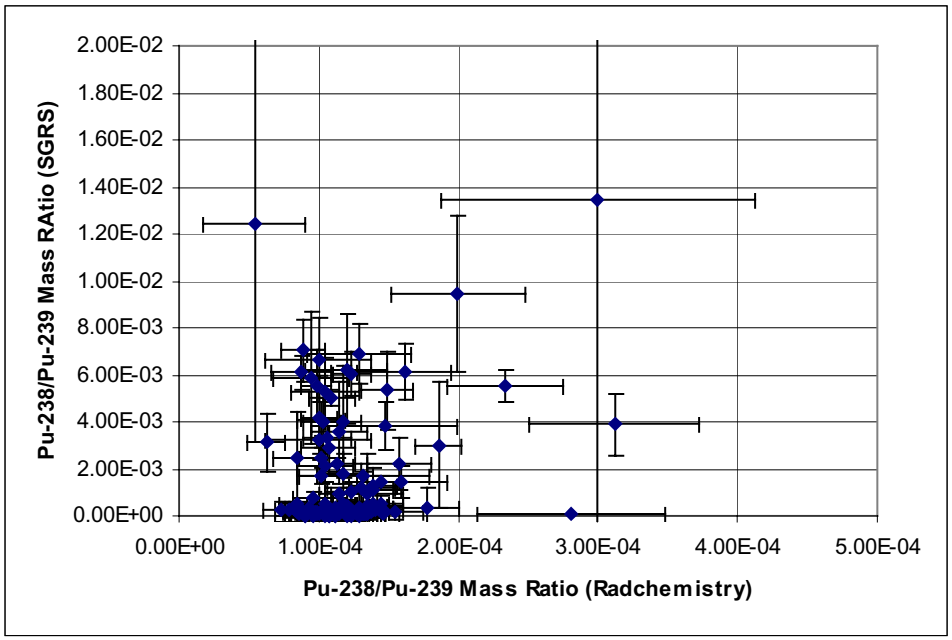

Figure 9 Comparison of destructive (Radiochemistry) versus NDA (SGRS) values for the $^{238}Pu/^{239}Pu$ mass ratio

U-235/U-238 Mass Ratios

Summary statistics are presented in Table 4. Figure 10 presents the frequency histogram while the destructive and nondestructive results are compared in Figures 11 and 12. Those comparisons drawn from uranium analyses with no analytical warning flags (See the $^{235}U/^{239}Pu$ results section for a discussion.) are identified in Table 4 and plotted in a separate comparison plot in Figure 12.

Table 4 Summary statistics for % recovery of the measured $^{235}U/^{238}U$ mass ratio

	All values	*Eliminate 1 high flyer*	*No Analytical Flags*
Mean	1.01E+02	6.03E+01	8.12E+01
Standard Error	4.10E+01	5.18E+00	4.23E+00
Median	6.81E+01	6.73E+01	8.64E+01
Mode	#N/A	#N/A	#N/A
Standard Deviation	3.18E+02	3.98E+01	1.69E+01
Sample Variance	1.01E+05	1.58E+03	2.86E+02
Kurtosis	5.81E+01	1.99E+00	3.74E+00
Skewness	7.56E+00	5.30E-01	-1.82E+00
Range	2.50E+03	2.10E+02	6.39E+01
Minimum	1.29E-01	1.29E-01	3.25E+01
Maximum	2.50E+03	2.10E+02	9.64E+01
Sum	6.06E+03	3.56E+03	1.30E+03
Count	6.00E+01	5.90E+01	1.60E+01

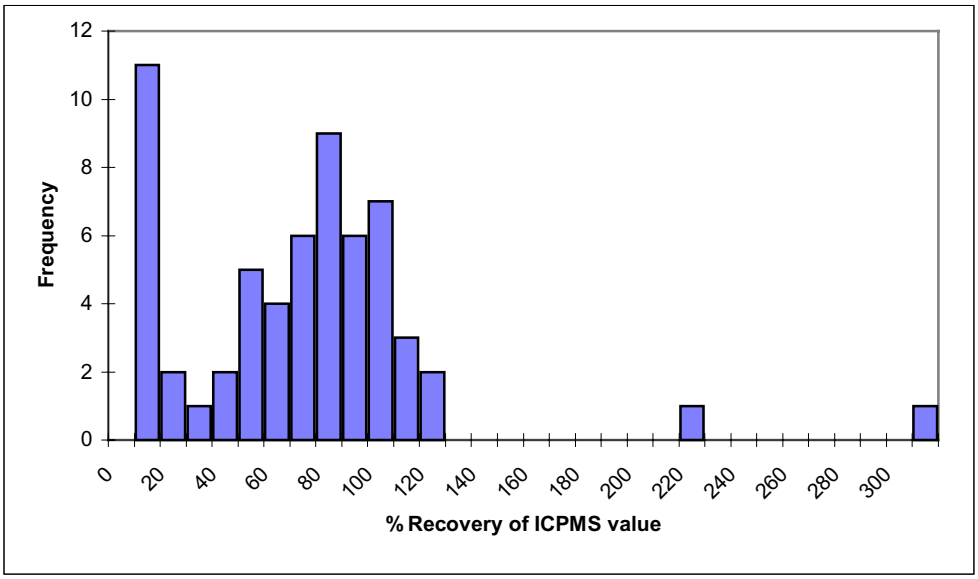

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Figure 10 Frequency distribution for % recovery of the measured $^{235}U/^{238}U$ mass ratio

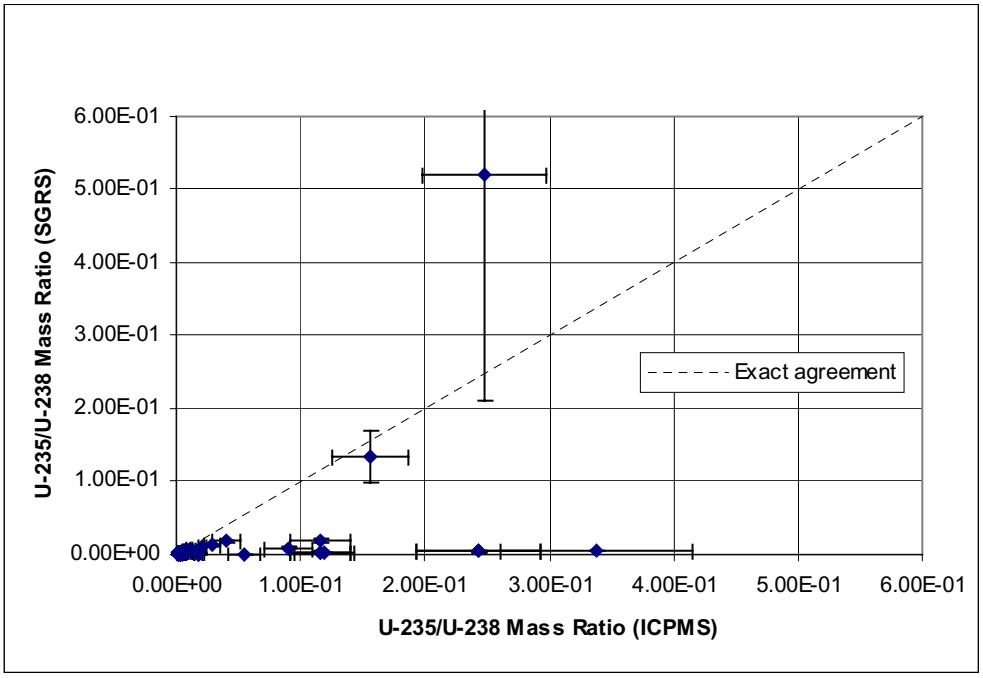

Figure 11 Comparison of the destructive (ICPMS) results and nondestructive (SGRS) results for the $^{235}U/^{238}U$ mass ratio. Positive values only. One high flyer was eliminated to simplify plotting.

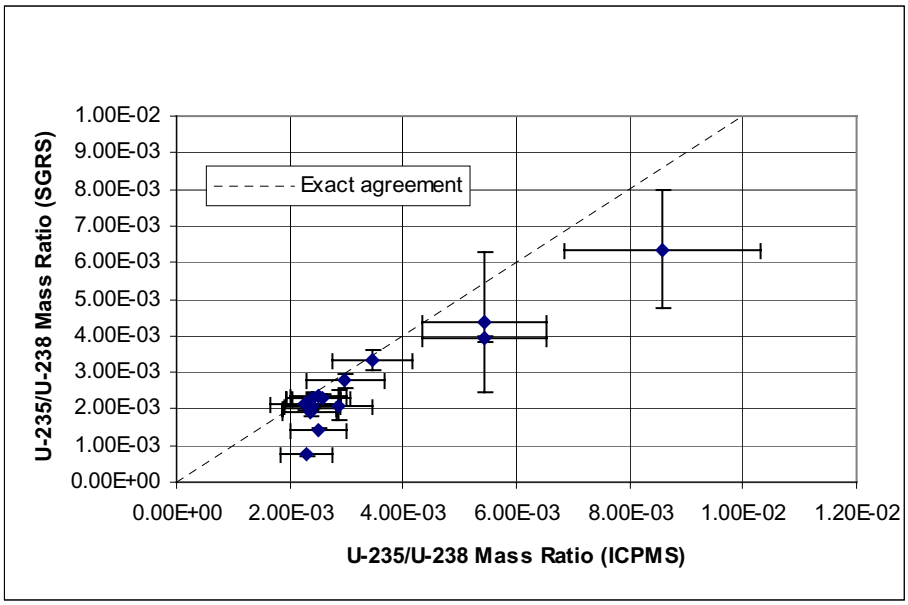

Figure 12 Comparison of the destructive (ICPMS) results and nondestructive (SGRS) results for the $^{235}U/^{238}U$ mass ratio for those ICPMS results with no analytical warning flags.

3.3 Discussion

The SGRS nondestructive measurements of the $^{241}Am/^{239}Pu$ mass ratios agree very well with the nondestructive results. Agreement between the nondestructive and destructive measurements of the $^{238}Pu/^{239}Pu$ mass ratios is very poor even taking into account the high uncertainties assigned to the SGRS results. The reason for this poor agreement is not understood; however, it seems likely that the problem is with the NDA rather than destructive analysis results. In SWEPP sludge drums the Pu is weapon's grade material. In WG Pu, the expected $^{238}Pu/^{239}Pu$ mass ratio is (1.6±0.85)E-04. Figure 9, which compare the destructive and NDA results for the $^{238}Pu/^{239}Pu$ mass ratio, shows the destructive radiochemical results strongly grouped between about 9E-05 and 1.8E-04 while the NDA results often exceed this range by orders of magnitude. The SGRS-measured Pu mass ratios are only used to confirm WG Pu, through a comparison of the $^{240}Pu/^{239}Pu$ and the $^{241}Pu/^{239}Pu$ ratios, poor performance on the $^{238}Pu/^{239}Pu$ mass ratio has little impact on the drum characterization results.

Problems with the destructive ICPMS results for uranium complicated comparisons for ratios of the uranium isotopes, both for $^{235}U/^{239}Pu$ and for $^{235}U/^{238}U$ mass ratios. However, generally good agreement was demonstrated when analytical results were selected to minimize the effect of destructive analysis problems.

4.0 THE SGRS AS A QUANTITATIVE ASSAY DEVICE

The availability of radiochemical assay results on the set of 128 sludge drums facilitated a scoping study to evaluate the possible use of the SGRS as a quantitative assay device for SWEPP waste drums. Presently, drums are counted in the SGRS to determine radionuclide isotopic ratios, and these ratios used to support quantification by the Passive Active Neutron (PAN) assay system. If even a portion of the waste drums could be assayed in the SGRS, throughput would be increased and drum handling decreased.

4.1 Methodology

The INEEL has relied extensively on verified MCNP modeling for studies on the PAN assay system.[6] Our experience with MCNP convinced us that with due care, the absolute assay efficiency of the SGRS could be properly modeled. Our approach was to generate absolute efficiency values for the major ^{239}Pu lines from the destructive assay results and our measured spectra on a small subset of the 128 destructively assayed drums. These efficiency values were compared with those calculated by MCNP modeling.

For the initial absolute efficiency curve development a subset of 14 core-drilled drums were selected at random as calibration standards. After selection, the acquisition and sampling conditions were investigated. Four drums were eliminated because of poor agreement between either the duplicate core results or the analytical replicates. (A $\chi^2/DF \leq 4.0$ from the weighted averaging was required.) During the SWEPP assay of the core-sampled drums, the SGRS had a detector failure; consequently most of these drums were assayed with three rather than four Ge detectors operating. The subset of 10 drums was further pared to select only those assayed with three detectors. This eliminated half of the remaining drums. Destructive and nondestructive assay results for the remaining five drums were used to compute gamma-ray efficiency values (in counts per source gamma) at the major ^{239}Pu gamma-ray energies of 129, 203, 345, and 413 keV. From these four values and knowledge of the expected shape, an efficiency curve was sketched, extrapolating the curve to 50 keV and to 2000 keV.

A gamma-ray efficiency curve for the SGRS was also calculated using MCNP. The source was assumed to be a 208-l drum filled to a height of 58 cm (68% full) with a homogeneously contaminated inorganic

Sludge A matrix. MCNP tracked photons from the source and tallied those with full energy deposition in the modeled Ge crystal.

4.2 Results

The extrapolated efficiency curve developed from the radiochemical results is compared with the MCNP-calculated curve in Figure 13. While the two curves agree within about 15%, the MCNP result is uniformly high. We believe this is due to the simplicity of the Ge detector modeling in MCNP.

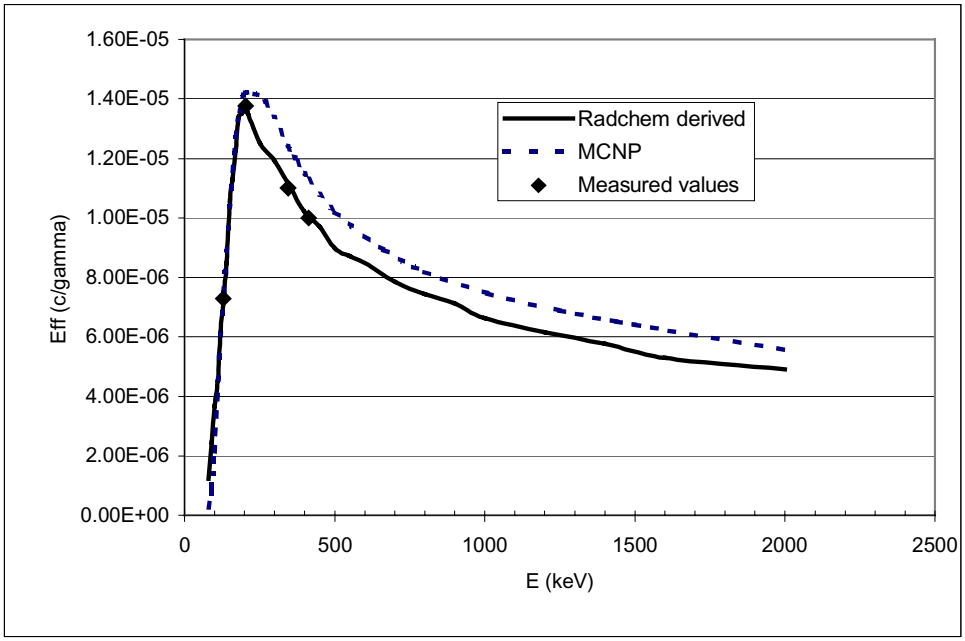

Figure 13 Comparison of the efficiency curve derived from the radiochemical results with that calculated by MCNP modeling.

The remaining drums from the sampled inventory were assayed using the radiochemically-derived efficiency curve. Since the curve was derived from drums using a given set of three detectors (2, 3, and 4) the test was confined to the 61 sampled drums that had also been assayed with the same three-detector set. Tables 5 and 6 present the summary statistics for the % recovery of the radiochemical values for ^{239}Pu and ^{241}Am respectively, Figures 14 and 15 show the distribution histograms while Figures 16 and 17 present the destructive versus SGRS assay comparisons. The error bars plotted for the SGRS data represent only the statistical fitting error.

Table 5 Summary statistics for the % recovery of the radiochemically-determined ^{239}Pu content of waste drums using an SGRS-based quantitative assay.

All Values	
Mean	106.6
Standard Error	5.2
Median	102.7
Mode	#N/A
Standard Deviation	40.7
Sample Variance	1656.7
Kurtosis	1.306
Skewness	0.337
Range	220.6
Minimum	4.0
Maximum	224. 7
Sum	6502.9
Count	61

Table 6 Summary statistics for the % recovery of the radiochemically-determined ^{241}Am content of waste drums using an SGRS-based quantitative assay.

2 very high flyers eliminated	
Mean	95.4
Standard Error	4.8
Median	92.6
Mode	#N/A
Standard Deviation	36.9
Sample Variance	1359.8
Kurtosis	3.79
Skewness	1.33
Range	223.0
Minimum	19.98
Maximum	243.0
Sum	5631.0
Count	59

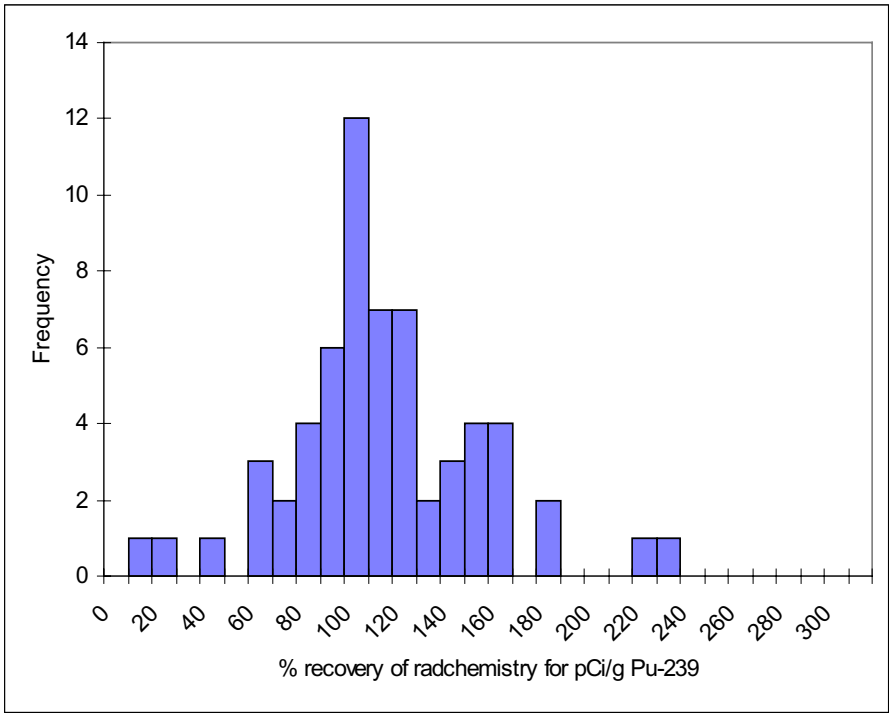

Figure 14 Distribution of % recovery of the radiochemically-determined ^{239}Pu content of waste drums using an SGRS-based quantitative assay.

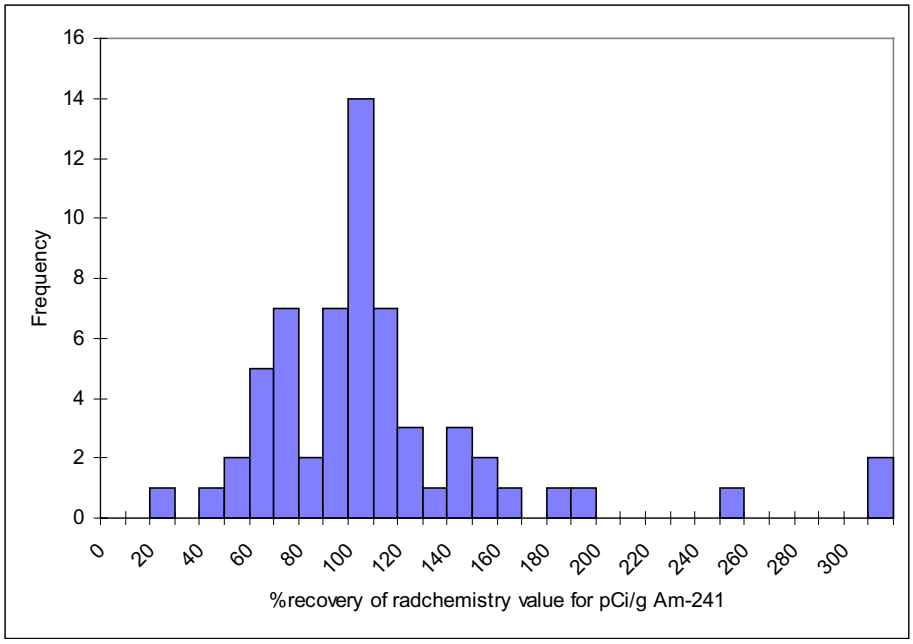

Figure 15 Distribution of % recovery of the radiochemically-determined ^{241}Am content of waste drums using an SGRS-based quantitative assay.

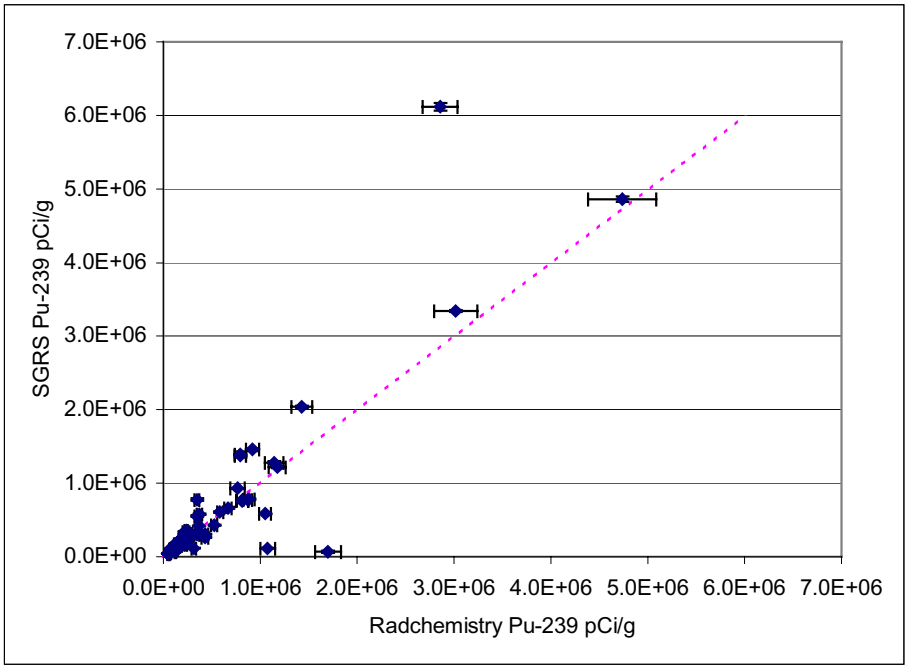

Figure 16 Comparison of the destructive and nondestructive (quantitative SGRS) results for ^{239}Pu concentration. All results are plotted.

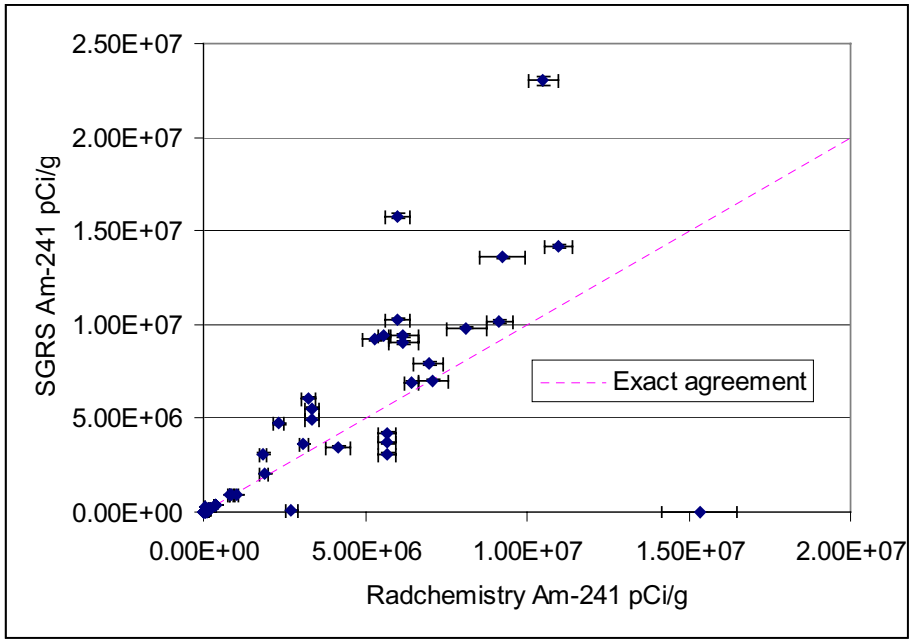

Figure 17 Comparison of the destructive and nondestructive (quantitative SGRS) results for ^{241}Am concentration.

4.3 Discussion

These scoping study results are very encouraging. On this limited data set, the SGRS quantitative assay gave a mean % recovery of the radiochemically-determined ^{239}Pu concentration of 107% with a relative standard deviation of about 40%. Similar, but somewhat lower results were obtained for ^{241}Am. There was no attempt to correct for differences in fill height or matrix density – fairly simple corrections that should improve the assay results.

5.0 SUMMARY AND CONCLUSIONS

Although the principal purposes for the destructive analysis of core samples from inorganic sludge drums were to aid in assessment of the measurement uncertainty for PAN quantitative assays,[1] and to gather information on RCRA listed hazardous components, these destructive assay results provided a unique opportunity to evaluate the performance of the SGRS. The destructive results for Pu, Am, and U mass ratios were compared with those determined during routine NDA measurements with the SGRS.

The SGRS performed well on determination of the ^{241}Am/^{239}Pu and ^{235}U/^{239}Pu ratios that are used routinely in the characterization of waste drums at SWEPP. The SGRS-measured ^{241}Am/^{239}Pu mass ratios gave a mean percent recovery of 102.7% of the destructive result with a relative standard deviation of 46%. Evaluation of the ^{235}U/^{239}Pu mass ratio results was complicated by destructive analysis problems. When 6 obvious "flyers" are eliminated from the data set, SGRS-measured ^{235}U/^{239}Pu mass ratios gave a mean percent recovery of 94% of the destructive result with a relative standard deviation of 40%. Selecting a smaller results set that had no destructive analysis warning flags gave a mean percent recovery of 74% of the destructive result with a relative standard deviation of 39%.

The SGRS results for the ^{238}Pu/^{239}Pu mass ratio did not agree with the destructive results. The reason for this poor agreement is not clear. Our SGRS analysis program and other nondestructive Pu isotopic codes (MGA and FRAM) give the same ^{238}Pu/^{239}Pu mass ratio results on inorganic sludge drums.[5]

As a preliminary assessment of the possibility of using the SGRS as a quantitative assay device for these inorganic sludge drums, we used a subset of the destructively analyzed drums to develop an absolute efficiency curve for the SGRS. This curve was uniformly higher than, but within about 15% of a curve calculated using MCNP modeling. When the SGRS spectra on the remaining drums were analyzed using the absolute efficiency curve, the quantitative results (in pCi/g) for ^{239}Pu and ^{241}Am were very

encouraging. The mean % recovery (relative to the radiochemical analysis result) for ^{239}Pu was 107% with a relative standard deviation of 40%, while similar results for ^{241}Am were 95% recovery with a relative standard deviation of 39%.

6.0 REFERENCES

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