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Np Analysis of Freshly Separated Material

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Abstract

Np analysis has historically relied upon the Pa/Np secular equilibrium for quantitative results. The Savannah River Site has recently undertaken a mission concerning Np. In this application, Np is separated from Pa, packaged, possibly mixed with other batches, and assayed. The fresh separation and mixing of batches prevents the use of the Pa133 prodigy peaks for assay. *This effort was a developmental project novel in the DOE complex.*

This paper will discuss the challenges encountered in the design of instrumentation to assay Np directly. The most abundant Np peak that is unfettered by Pa prodigy, Am, or other SNM materials is the 29.6keV. Quantitative measurement of such a low energy peak presents significant problems with attenuation, Compton effects, and other such issues that arise while trying to maximize the effects of low energy peaks.

The solutions rely on exploiting the “tried and true” methods with regard to shielding, detector technology, and calibration techniques, but with a very low energy perspective. The results are intriguing and, with some assumptions regarding sample homogeneity, quantitative within normal MC&A statistics.

INTRODUCTION

The Savannah River Site (SRS) is in the process of initiating a new mission for Np purification. In this process Np is separated from other isotopes. There are two main assay streams: process solutions and glovebox waste (floor sweepings, HEPA filters, and other process waste items). As with other materials, quantitative NDA is required for this process. Np analysis has historically relied upon the $^{233}\text{Pa}/^{237}\text{Np}$ secular equilibrium for quantitative results.

^{233}Pa 's peak is a very robust peak and allows for good assay results. ^{233}Pa 's half-life is 27 days. A general rule-of-thumb is that equilibrium is established after 6-7 half-lives, or ~ 6 months for the $^{237}\text{Np}/^{233}\text{Pa}$ equilibrium. Operations requires analysis before this equilibrium can be established. Further, Operations may mix batches and is not able to accurately track the date of separation or relative quantities of these mixed batches. This precluded the use of the

Table 1 - The Twenty most Intense γ -rays Arising from ^{237}Np

Sorted by energy		Sorted by branching ratio	
Energy (keV)	Branching Ratio (%)	Energy (keV)	Branching Ratio (%)
29.38	9.8	86.49	13.1
46.6	0.14	29.38	9.8
57.11	0.42	95.87	2.96
62.9	0.2	92.29	1.82
71	0.5	108	1.02
86.49	13.1	94.66	0.84
88.1	0.16	71	0.5
92.29	1.82	143.25	0.473
94.66	0.84	57.11	0.42
95.87	2.96	111.5	0.35
106.3	0.105	151.41	0.263
108	1.02	194.97	0.21
111.5	0.35	62.9	0.2
117.72	0.184	117.72	0.184
131.11	0.112	212.33	0.184
143.25	0.473	88.1	0.16
151.41	0.263	46.6	0.14
155.25	0.105	131.11	0.112
194.97	0.21	106.3	0.105
212.33	0.184	155.25	0.105

$^{237}\text{Np}/^{233}\text{Pa}$ equilibrium for quantitative analyses of ^{237}Np . This set of production circumstances required that analysis be based on data arising directly from ^{237}Np and not any equilibrium products.

There were several considerations when establishing the optimal assay peak: peak intensity for better counting statistics; higher energy for minimization of transmission corrections; and, interferences from other γ -rays. Table 1¹ presents ^{237}Np 's 20 most abundant g-rays. Figure 1² shows the effects of energy vs. peak attenuation for various materials. Although attenuation can be an issue for process solutions, it becomes more of an issue for the variety glovebox wastes and their packaging. Although attenuation is an issue, the 29.38 keV γ -ray was selected for assay as it was the most intense peak without interferences. *It should be noted that this effort was a developmental project novel to the DOE complex.*

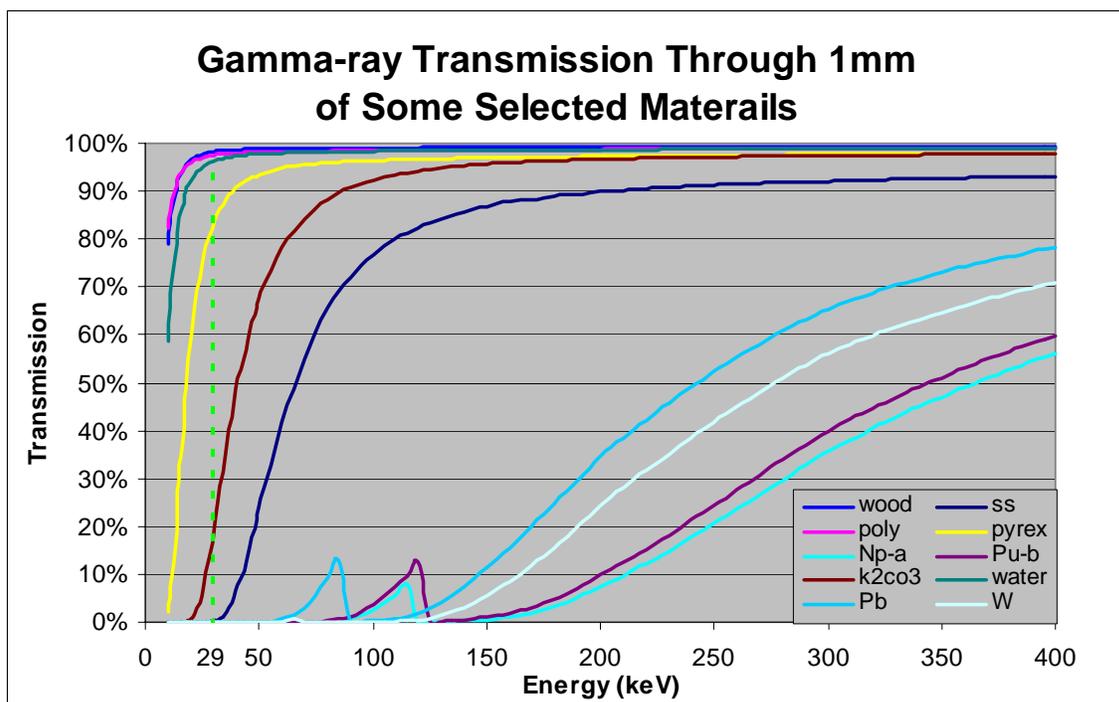


Figure 1 – γ -ray Transmission Through 1mm of some Selected Materials

Figure 2 is a ^{237}Np spectrum demonstrating the robustness and freedom from competing γ -rays of ^{237}Np 's 29keV peak. The peak on the far left is the 29keV ^{237}Np peak and the one on the far right is the ^{233}Pa 312keV peak. The light green is the ^{237}Np spectrum and the cyan is the

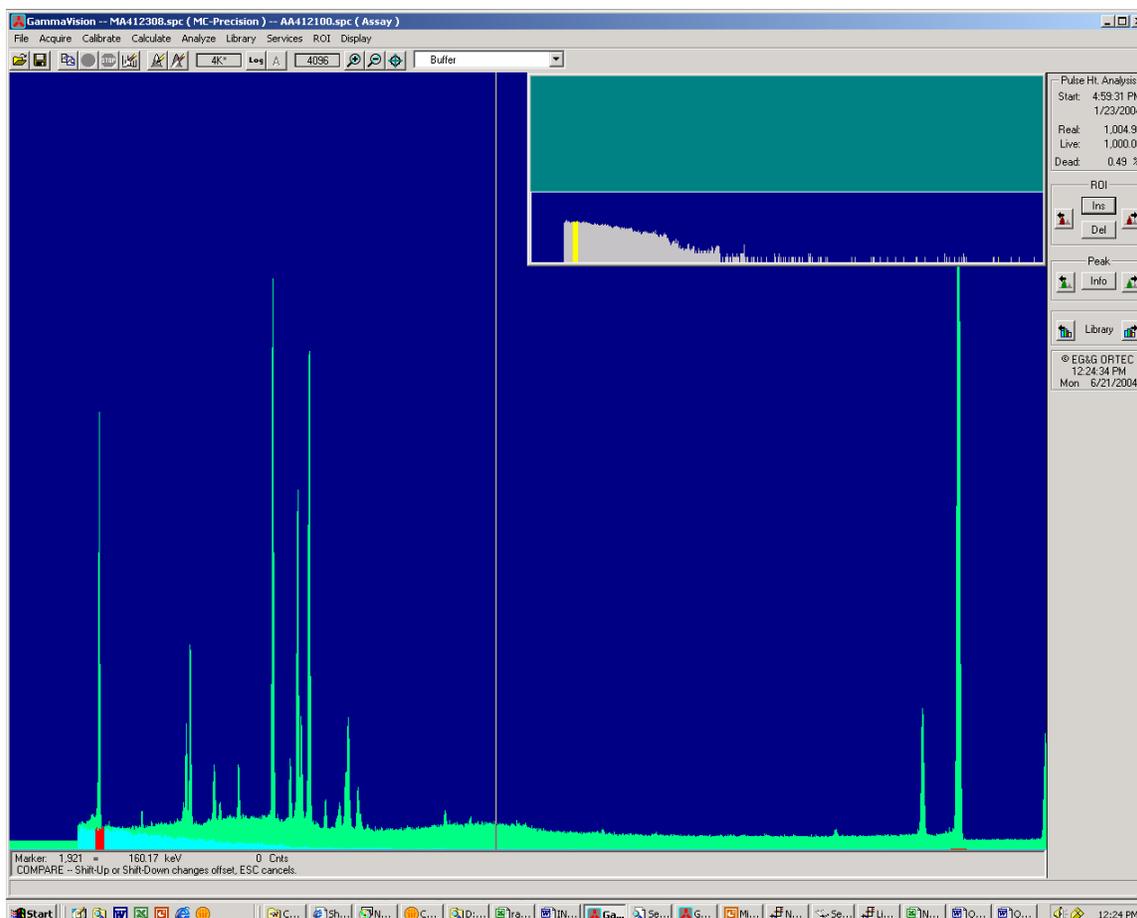


Figure 2 – ^{237}Np Spectrum with Overlaid Background.

associated background. Separation from other peaks, peak intensity, and background are all very good.

^{237}Np CALIBRATION

As a result of the discussions in the introduction section above regarding the difficulty in the assay of low energy peaks, the calibration for ^{237}Np is less straight forward. As the standards used for this calibration were fabricated from older material (i.e., where the $^{233}\text{Pa}/^{237}\text{Np}$ equilibrium is well established), the interference from ^{233}Pa is very pronounced. With items fresh from separation, this interference will be reduced, improving the quality of ^{237}Np analysis. Therefore, the results presented in this report are most likely worst cases and it is expected that analysis of freshly separated material from HB-line processes will be of higher quality (lower error). Again, this is very sensitive to packaging and matrix effects.

²³⁷Np Bearing Solutions^{3, 4}

For solutions, calibration is simpler. Figure 3 is a plot of the compiled calibration data for Np bearing solutions.

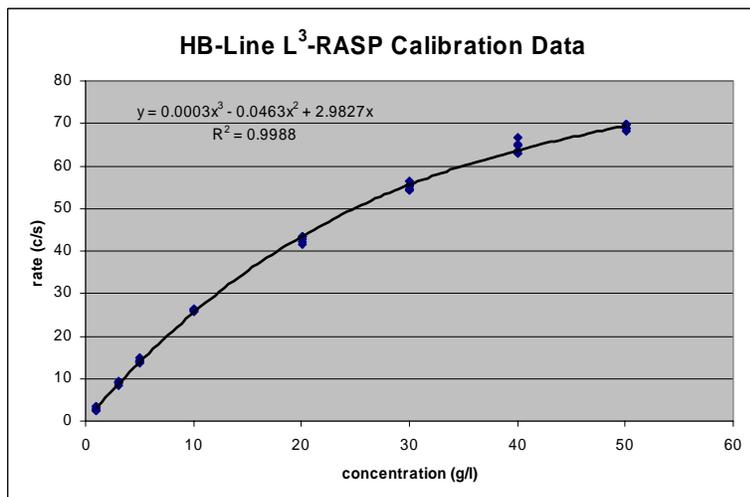


Figure 3-- Plot of ²³⁷Np Calibration Data for Solutions

Although the plot is not linear due to self-attenuation of the Np, it is predictable and can readily be handled with a quadratic calibration curve. Since solutions are relatively pure and homogeneous, self-attenuation for metal other than Np or inhomogeneity is significantly less of an issue as it is for glovebox waste.

Uncertainties Associated with Quantitative Measurements of

²³⁷Np Bearing Solutions

Figure 4 is a plot of the observed error vs. solution concentration of the calibration standards for the 29keV peak. The red line is the relative error expressed in percent. As expected, relative errors significantly decrease as concentration (i.e. count rate) increases. The blue is a plot of the accepted value vs. the observed. It demonstrates agreement between standard values and calculated results. The expected relative uncertainty at lower concentrations (1-3 g/l) is ~ 6%, while at higher concentrations the instrument can provide results as good as ~3%. These errors are significantly greater than are normally observed for Pu analysis. The counting statistics for the quantitative assay of the Np 29keV peak are much poorer for the reasons discussed in the introduction.

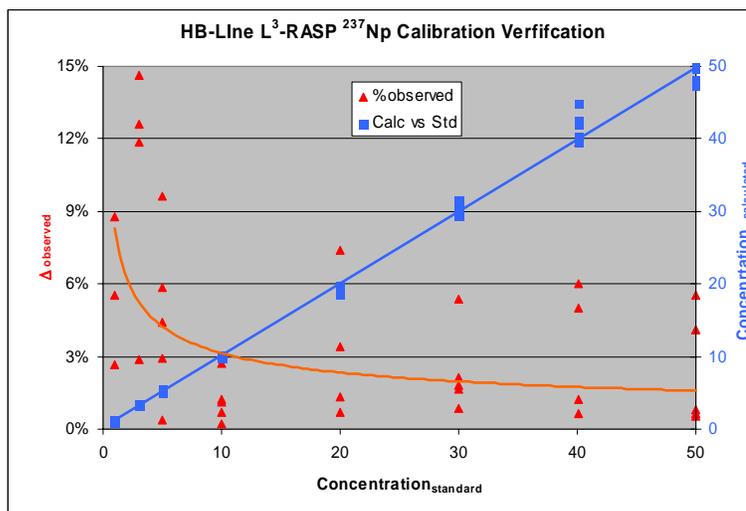


Figure 4-- Plot of the Errors Associated With the Calibration of ²³⁷Np Bearing Solutions

These plots demonstrate a well behaved calibration and errors within acceptable MC&A limits.

Figure 5 and Figure 6 are photographs of the solution instrumentation used for this report. The shielding for this instrument allows for very low backgrounds³. It is constructed of 4" of tungsten in 4π geometry.



Figure 5 – Sample Shield for Solution Assay of ^{237}Np Bearing Solutions

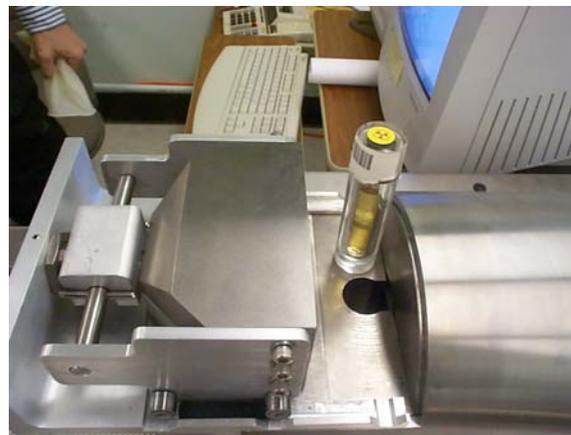


Figure 6 – Sample and Open Sample Shield for Solution Assay of ^{237}Np Bearing Solutions

^{237}Np Glovebox Waste⁵

Due the arguments presented above with regard to assay peak energy and attenuation, glovebox waste is more difficult. Glovebox waste is normally inhomogeneous, packed irregularly and contains one or more “hot spots” somewhere in the container. There are often significant differences throughout the container with regard to attenuation properties. As a result, attenuation effects must be measured and corrected for each individual assay item.

For the analysis of glovebox waste, quantitative assay of very-low energy peaks, such as ^{237}Np 's 29keV peak, is fraught with many difficulties. Low energy γ -rays are significantly absorbed by various materials as demonstrated in Figure 1². This figure represents a wide variety of materials with varying absorption capacities. Note that all materials affect the 29keV region peak somewhat. The ability of a material to absorb γ -rays is proportional to the natural logarithm of its thickness. That is, for every doubling of material thickness, the transmission is reduced by 0.69 ($\ln 2$). It is this varying absorption of the 29keV peak by unknown matrix materials that makes the assay of freshly separated ^{237}Np so difficult. In an attempt to correct for this, the instrument measures the absorption of three peaks (^{241}Am @ 59keV, ^{133}Ba @ 356keV, and ^{137}Cs @ 662keV) and extrapolates to 29keV in an attempt to calculate the effects of matrix material and container upon the assay of the 29keV of ^{237}Np . As there are no bounding transmission peaks (i.e. none at or below the 29keV peak), this extrapolation introduces significant errors. As the measured absorption becomes greater, this correction factor grows exponentially, also adding additional very significant errors. The figure shows how even relatively minor amounts of attenuating materials (1mm) can affect assay results by order of magnitudes.

To assay the required four different isotopes (^{238}Pu , ^{239}Pu , ^{235}U , and ^{237}Np) many compromises were required. Self-absorption of γ rays by dense matrix material, as described earlier in this report, is more of an issue for the low energy ^{237}Np gamma analysis of freshly separated material than in any other application at SRS. This also required the introduction of a low energy transmission source (^{241}Am was selected). Segregation of waste for density effects (primarily any metals), isotopes (^{237}Np can block the ^{239}Pu signature; the ^{241}Am decay product from Pu will compromise the transmission correction for ^{237}Np analysis), and knowledge of packaging are all significantly more important for this application. Further, it was recommended that different assay protocols be employed based on the knowledge of packaging. The important aspects of this

“process knowledge” are 1) relative activity density (single point source vs. a more homogenous mix throughout the item); 2) packaging of denser materials (primarily any metals); and 3),

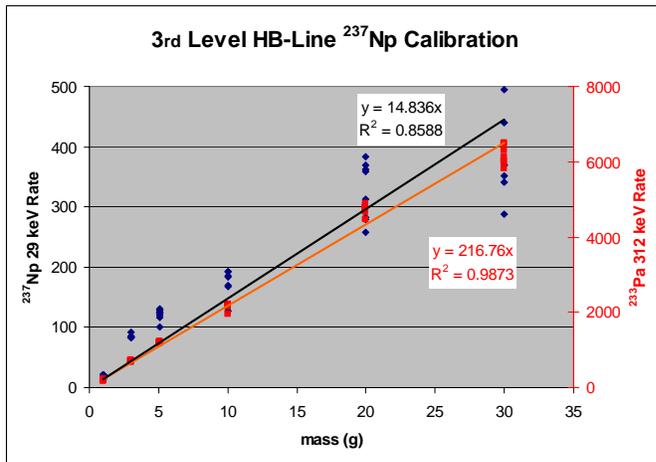


Figure 7– Plot of the ²³⁷Np Calibration Data

312keV peak is significantly more robust and its matrix attenuation correction contains less error. As the figure shows, the results for the 312keV peak ($R^2 = 0.98$) better fits the data than does the 29keV data ($R^2 = 0.85$).

To further validate the calibration of the instrument, the observed errors were plotted relative to the calculated mass. This plot is presented in Figure 8. Note that the errors for the ²³³Pa peak in red are significantly lower than those for the 29keV peak, supporting the calibration

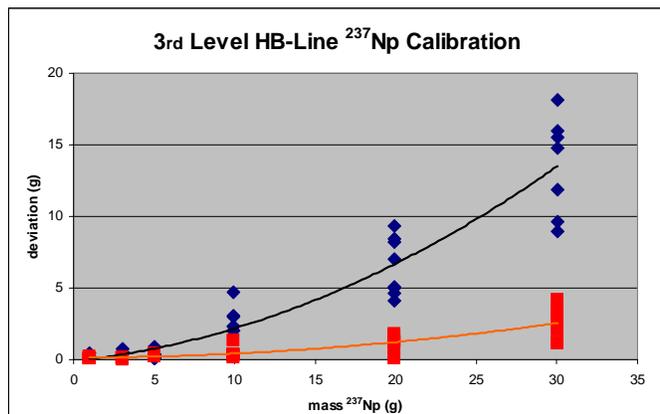


Figure 8– Observed Deviation from Accepted Values for ²³⁷Np

determination that the 312keV peak should be used under the stated criteria. It is also notable that the spread of repeated observations of the same standard is significantly greater for the 29keV peak. This larger spread of data is the cause of the increased error component of the 29Kev data as compared to the 312keV data.

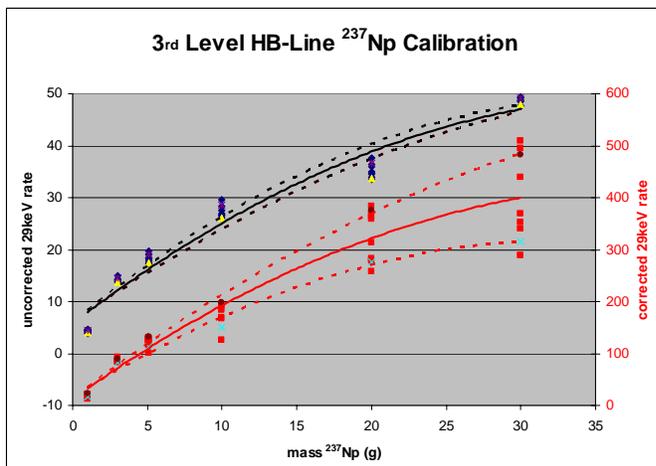


Figure 9– Error Comparison Between Raw Count Rate and Transmission Corrected Count Rate

knowledge of suspected isotopes (interferences as stated above) are the basis of the selection of the appropriate assay protocol.

Figure 7 presents a plot of the ²³⁷Np calibration data for both the ²³⁷Np 29keV peak and the progeny product, ²³³Pa 312keV peak. The R^2 statistic is a measure of degree of fit (correlation) between rate and mass, with 1.00 indicating a perfect fit. The red line represents the 312keV data and the black the 29keV data. As discussed, with the calibration standards at equilibrium, the

Figure 9 numerically demonstrates the matrix attenuation correction problem. As a reminder, the calibration standards are homogeneous, Np being the only significant attenuating material. Armed with this fact, the raw uncorrected count rate can be plotted. It is expected that this rate would fall off exponentially as the mass increases (more Np relates to less count rate/gram as increasing Np absorbs a larger proportion of the γ -rays). The black line represents the raw rates with

the observed deviations plotted by the black dashed lines. The red line represents the transmission corrected rates. Note the larger differences for corrected data vs. the uncorrected data.

If assay items could be guaranteed to contain only Np in low attenuating matrices, then using the uncorrected rates would produce significantly better results. This would require a guarantee that the item contained only plastics, paper, and other low density materials. The item could contain no possibility of leaded gloves, steel, significant quantities (greater than a few grams) of other SNM, or any other combination of items that might prove too dense to allow the unimpeded emission of the 29keV γ -ray. That would be a very poor assumption for waste items leaving HB-line. Therefore, the transmission corrected rate, even with its poor uncertainties, is the only realistic result that can be used.

Figure 10 is a photograph of typical glovebox waste instrumentation. Shown on the right is the transmission source shield and shutter, the sample turntable in the center, and the LEGe detector shield and collimator to the left.



Figure 10 -- Photograph of Glovebox Waste Instrumentation

As discussed in the introduction, the assay of ^{237}Np using the 29keV is extremely sensitive to matrix absorption (materials such as trash, gloves, and other materials mixed in the item to be assayed for ^{237}Np). The peak from the progeny product, ^{233}Pa , is not as sensitive (see Figure 1). The 312keV calibration constant represents the quantity of ^{237}Np in the item of aged material (i.e., at equilibrium). As the 312keV peak is significantly stronger and not subject to the magnitude of matrix attenuation problems, it is an excellent assay peak for materials at or nearing equilibrium. Ideally, at equilibrium, the results from the 29keV peaks and from the 312keV should be statistically the same. At times significantly prior to equilibrium, the 29keV peak best represents the quantity of ^{237}Np in an item with minimal self-absorption problems. Depending upon specific circumstances (packaging, quantity, matrix materials), the 312keV peak from ^{233}Pa may provide the most realistic result for items as “young” as 1 month (50% $^{233}\text{Pa}/^{237}\text{Np}$ equilibrium has been established at 1 month). The dilemma is to determine just when to use one assay over the other. It is the recommendation of this report to use the assay result that reports the greater quantity of ^{237}Np with the caveat that the 29keV correction is valid. Often, with items containing absorbing materials and nearing equilibrium, the correction for the 29keV may be valid, but with a very large uncertainty associated with it. This large uncertainty could cause an under-correction. Under these circumstances, the 312 peak would provide the more realistic result.

The observation of increasing error with increasing count rate (increasing mass) is contrary to intuition. This phenomenon is caused by the increasing error in matrix attenuation correction as elaborated upon in previous discussions. That is, contrary to the norm, the increase in statistics (lower uncertainty) with high mass is overshadowed by the increasing errors matrix correction. To reiterate, this only occurs when low energy assay peaks are used. *This point is belabored as it is the overriding issue in ^{237}Np analysis of freshly separated materials.*

Uncertainties Associated with Quantitative Measurements of ^{237}Np Glovebox Waste

All the discussion thus far leads to the conclusion that measurement uncertainties will be higher than those observed for other SNM or for aged ^{237}Np than when attempting to quantify Np using the 29keV peak. Contrary to typical NDA techniques, increasing uncertainties will be observed with increasing mass. The uncertainties associated with the 312keV peak are significantly better. The results for the 312keV peak should be used whenever possible.

When the 29keV is used, expected errors are in the range of 10% for acceptable transmission corrections and Np masses in the 1-20 gram range. In the 20-30 gram range and with items exhibiting significant self-attenuation, errors can be expected to be higher until the point where the assay results can no longer be accurately transmission corrected as signified by outrageous uncertainties.

CONCLUSIONS

The data and results reported in this document demonstrate an instrument operating within expected limits for the assay of ^{239}Pu , ^{238}Pu , ^{235}U and ^{237}Np . Typical MLDs⁶ have been calculated and can be expected to be significantly less than 1 gram for each isotope. Uncertainties are the larger question for ^{237}Np assay using the 29keV peak. They will vary significantly with minor perturbations in sample matrix. With little matrix attenuation affects, uncertainties can be expected in the range of 10% for freshly separated material and 5% or lower for aged material. For ^{239}Pu , ^{238}Pu , and ^{235}U 2σ errors are estimated to be in 3 to 5% range. It should be noted that these errors are only the errors arising from calibration of very well characterized standards. Packaging, matrix effects, and other operational issues will further increase these errors.

To incorporate these four different isotopes (^{238}Pu , ^{239}Pu , ^{235}U , and ^{237}Np) many compromises were required. Self-absorption of γ rays by dense matrix material, as described earlier in this report, is more of an issue for the low energy ^{237}Np gamma analysis of freshly separated material than in any other application at SRS. This also required the introduction of a low energy transmission source (^{241}Am was selected). Segregation of waste for density effects (primarily any metals), isotopes (^{237}Np can block the ^{239}Pu signature; the ^{241}Am decay product from Pu will compromise the transmission correction for ^{237}Np analysis), and knowledge of packaging are all significantly more important for this application. It is recommended that different assay protocols be employed based on the knowledge of packaging. The important aspects of this "process knowledge" are 1) relative activity density (single point source vs. a more homogenous mix throughout the item); 2) packaging of denser materials (primarily any metals); and 3), knowledge of suspected isotopes (interferences as stated above) are the basis of the selection of the appropriate assay protocol.

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