Challenges and Recent Developments of Neutron Non-Destructive Assay with UO2F2-Bearing Materials – 17336

Marcel Villani *, Brent Montgomery **
* Mirion Technologies (Canberra), Meriden, CT
** Fluor Federal Services Paducah Deactivation Project (FPDP), Kevil, KY

ABSTRACT

In the enrichment process of an operating Gaseous Diffusion Plant (GDP), such as the Portsmouth and Paducah facilities, UF6 gas will immediately hydrolyze forming the chemical compound UO_2F_2 (Uranyl Fluoride). This mostly happens in Alumina (Al_2O_3) traps where the UF_6 adsorbs to moistened Alumina pellets forming a UO_2F_2 layer around the pellet. Similarly, NaF ·UF_6 absorption traps produce the complex Na_2UF_8 which also hydrolyzes when exposed to moist air. UO_2F_2 can also be formed in many other processes where UF_6 gas comes into contact with moisture within structures and objects such as pipes, converters compressors and coolers. When the structures are refurbished, or designated for D&D, UO_2F_2-bearing objects are generated both in situ and ex situ requiring fissile (U-235) characterization. In addition, ex situ waste streams are generated when UO_2F_2-bearing materials are placed in drummed or boxed waste containers. Gamma spectroscopy Non-Destructive Assay (NDA) is commonly utilized to characterize UO_2F_2-bearing waste but generally has high associated Total Measurement Uncertainties (TMU's) and, in some cases, Data Quality Objectives (DQO's) cannot be met. In addition, high UO_2F_2 mass loadings, such as hold-up materials, require gamma modeling when infinitely thick to the Uranium energy lines. A common neutron NDA technique, or method, is to exploit the neutrons generated from the F-19(α, n)Na-22 reaction which has an appreciable reaction cross-section. The isotopes of Uranium are α-emitters, and, in particular, U-234 has a significantly higher α-decay reaction cross-section leading to a significant relative neutron Specific Activity (nSA). Neutron NDA is appealing since, in some cases, it has potentially lower TMU's than gamma NDA and neutron detector slabs facilitate surrounding large, complex-shaped, objects. Characterizing UO_2F_2-bearing waste for fissile content using neutrons generated from U-234, requires the U-235/U-234 ratio as well as the enrichment as well as the corresponding nSA's. It is also noted that U-238 has a considerable, relative, spontaneous fission nSA and this is a higher concern for low-enrichments where the mass of U-238 dominates. Additional neutron interfering elements include cosmic-ray induced spallation within the objects and background from other, in situ, UO_2F_2-bearing objects. In this paper we present the challenges and recently developed hardware and algorithmic strategies for quantifying fissile mass both in situ and ex situ using neutron NDA that works in conjunction to gamma spectroscopy NDA, or process knowledge, for objects and drummed/boxed waste containing UO_2F_2-bearing materials leading to minimal TMU's and achievable DQO's.

INTRODUCTION

In the enrichment process of an operating Gaseous Diffusion Plant (GDP), such as the

Portsmouth and Paducah facilities, UF6 gas will hydrolyze with H2O forming the chemical compound UO2F2 (Uranyl Fluoride). This mostly happens in Alumina traps where the UF_6 as adsorbs to moistened Alumina pellets forming a UO_2F_2 layer around the pellet. UO_2F_2 can also be formed in many other processes where UF_6 gas comes into contact with moist air within structures such as pipes, converters compressors and coolers. When the structures are refurbished or designated for D&D, UO_2F_2 waste streams are generated and placed in drummed or boxed waste containers. The objective is then to produce NDA methods to quantify the enrichment and U-235 mass content, with associated TMU, for the drummed and boxed waste containers.

A common NDA technique, or method, is to exploit the neutrons generated from the F-19(α, n)Na-22 reaction which has an appreciable reaction cross-section. The isotopes of Uranium are α-emitters, and, in particular, U-234 has a significantly higher α-decay relative specific activity [1] as shown in Table II. It is also noted that U-238 has an appreciable spontaneous specific activity and this is a concern for low-enrichments where the mass of U-238 dominates.

The purpose of this paper is to develop the method for utilizing neutrons generated from the F-19(α, n)Na-22 in UO_2F_2-bearing material and calibrating such as a function of U-234 mass. The second objective of this paper is to determine the method for using the U-234 mass calibration to determine the U-235 mass for a neutron signal measured from an unknown waste stream.

The calibration method will require known, NIST traceable, Working Reference Materials (WRM's) and the assay process of unknown waste streams will require, at a minimum, isotopics and/or gamma assay. This paper will assume that there will be the possibility of a gamma modality available as input to the neutron method. It is assumed that the gamma modality produces U-235 and U-238 mass via declared or measured isotopics or both nuclides are measured directly.

Table I Alpha and spontaneous fission specific activities of Uranium isotopes of interest in the GDP enrichment processes [1].

Isotope	Alpha Specific Activity (Ci/g)	Spontaneous Fission (n/s/g)
U-234	6.3x10-3	5.02x10-3
U-235	2.2×10-6	2.99x10-4
U-238	3.4×10-7	1.36x10-2

Portsmouth B-25 Box Monitor

The neutron methods developed in this document were applied to a recent Non-Destructive Assay System (NDA) co-developed at the Portsmouth Gaseous

Diffusion Plant in Piketon Ohio. The objective is not to fully describe the calibration and confirmation process for the Portsmouth NDA instrument but to embellish on the neutron methods described in this paper as they are applied to the Portsmouth NDA instrument. The NDA instrument is designed for assaying B-25 boxes loaded with primarily Dry Active Waste (DAW) with a small fraction of metals. Currently the instrument is located in building XT-847 where the enrichment range is limited to less than 20%.

The Building XT-847 B-25 box monitor consists of 4 Canberra BEGe 5030 detectors mounted in 90 degree ISOCS collimators and two 16.5" W x 31 ¾" H x 6 ½" D neutron slab counters with 8 atmosphere He-3 tubes (four 1" x 12" tubes each). The neutron detectors have 2" of HDPE shielding on all sides except the side facing the B-25 box. The basic arrangement of the box counter is shown in Fig. 1. The NDA instrument is calibrated for assay of Uranium for both gamma, via detector efficiency for U-235 and U-238, and neutron, via U-234 mass, assuming UO_2F_2 (Uranyl Fluoride) as the sample type, cellulose as the matrix type and Al_2O_3 (Alumina) as the material type. The neutron side will exploit the U-234 alpha emission in conjunction to the relatively high alpha-n cross-section of Fluorine and that the U-235 enrichment is a known function of the U-235/U-234 ratio at the enrichments expected in Building XT-847 (2% - 20%). The gamma side utilizes the U-235 gamma rays for low self-absorbing material types and the U-238 lines for high self-absorbing materials.

Two (opposing) neutron slab detectors were supplied by the Ports facility. The outer dimensions of the two slabs are 16.5" W x 31.75" H x 6.5" D. There is 2" of HDPE shielding on all sides except for the front (facing the B-25 box). The signal pulse width of each neutron detector was adjusted so as the output pulse was trimmed to 100 ns of width. The signal neutron slab signal ouputs are sent to an active circuit summation box. The summed signal output of the summation box was sent to the signal input of the Canberra JSR-15 coincidence (shift register) analyzer. A low-voltage (5 V) distribution box and high-voltage (SHV) distribution box were utilized to supply the low- and high-voltages to the slab detectors. A high-voltage plateau study was conducted for the summed output and was determined to be 1725 V. The preamp threshold was adjusted by the Ports NDA engineers so as to facilitate 100% gamma rejection for the anticipated activity range of the waste stream.

The Paducah facility is also in the process of constructing a B-25 box monitor but this instrument will be neutron only (4 slabs; two each opposing) with no gamma modality. The enrichment range is limited at the entire Paducah site (less than 5.5%) and the plan is to utilize the AK (Acceptable Knowledge) for enrichment for waste matrix within each B-25 container.

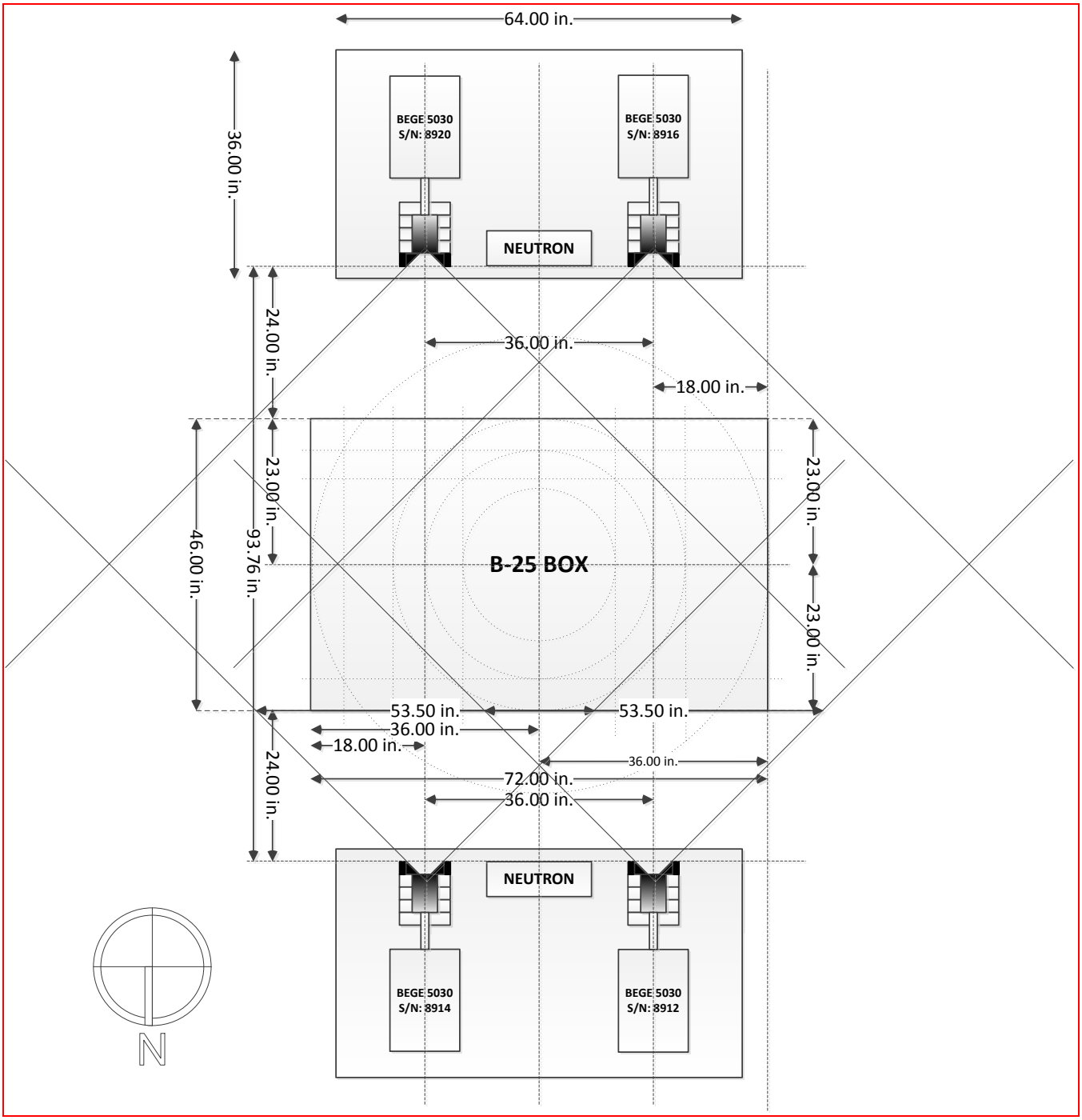

Fig. 1. The B-25 box monitor arrangement (overhead view) located in building XT-847 at Fluor-B&W Portsmouth.

METHODS

The known, published and computed values for UF_6 and UO_2F_2 nSA for the F-19(α,

n)Na-22 reaction are shown in Table II for the Uranium isotopes of interest for the GDP enrichment processes. The UF6 nSA and the U-234 and U-238 UO2F2 nSA, wet and dry, are from the literature [2]. The U-235 nSA is not available from the literature so it was computed, using a weighted mean method, from the ratios of UF6/UO2F2 nSA for both wet and dry.

Table II Neutron Specific Activities (nSA) for the F-19(α,n)Na-22 reaction for the Uranium isotopes of interest. The UF6 nSA and U-238 and U-234 UO2F2 nSA are from the literature [2]. The U-235 nSA and associated uncertainty are computed (weighted mean) from the UF6/UO2F2 nSA ration of U-234 and U-238.

U Nuclide	UF_6 nSA (n/s/g)	UO_2F_2 (wet)		UO_2F_2 (dry)	
		nSA (n/s/g)	UF6 Ratio	nSA (n/s/g)	UF6 Ratio
U-234	576 ± 42	172.8 ± 9.3	3.30	223.6 ± 12.1	2.58
U-235	0.122 ±0.009	(0.0345 ± 0.0025)†	(3.54)†	(0.0445 ± 0.0033)†	(2.74)†
U-238	0.0143 ± 0.002	0.00369 ± 0.00020	3.88	0.00474 ± 0.00029	3.02

† Computed from the weighted mean of the U-234 and U-238 UF6/UO2F2 nSA ratios.

In general, the observed (measured) system neutron rate, r, is defined as,

$$r = (nSA_{234} \cdot m_{234} + nSA_{235} \cdot m_{235} + nSA_{238} \cdot m_{238}) \cdot \epsilon_{\alpha,n} + nSFY_{238} \cdot m_{238} \cdot \epsilon_{SF} \qquad \text{Eq. 1}$$

Where nSA_{23x} is the neutron specific activity, n/s/g, for U-23x $^{19}F(\alpha,n)^{22}Na$ reaction within UO2F2 material and m_{23x} are the associated masses (grams) . We have also made the assumption that the energy distribution is approximate enough between the nSA $^{19}F(\alpha,n)^{22}Na$ for the isotopes of Uranium. If we further assume that the efficiency, ϵ_{SF}, of the higher energy SF neutrons can be approximated [3] by that of U-238 $^{19}F(\alpha,n)^{22}Na$ neutrons using a factor of 1.11 the measured rate becomes,

$$r = \left(nSA_{234} \cdot m_{234} + nSA_{235} \cdot m_{235} + nSA_{238} \cdot m_{238} + \frac{nSFY_{238}}{1.11} \cdot m_{238}\right) \cdot \epsilon_{\alpha,n} \qquad \text{Eq. 2}$$

Rewriting,

$$r = \left(m_{234} + \frac{nSA_{235}}{nSA_{234}} \cdot m_{235} + \frac{nSA_{238} + \frac{nSFY_{238}}{1.11}}{nSA_{234}} \cdot m_{238} \right) \cdot nSA_{234} \cdot \epsilon_{\alpha,n} \quad \text{Eq. 3}$$

Substituting,

$$\omega_{234} = nSA_{234} \cdot \epsilon_{\alpha,n} \quad \text{Eq. 4}$$

Yields ω_{234} which is the desired calibration parameter for U-234 mass as a function of the observed/measured count rate, r.

U-234 Mass Calibration

The calibration process involves assaying known UO2F2 standards in an empty container. The empty container is necessary since it will scatter neutrons and potentially moderate the efficiency observed at the neutron detectors. The rates must first be corrected for environmental background; environmental backgrounds should bound, for each day, the series of mass calibration measurements.

The calibration measurements and WRM's (Working Reference Materials) should be representative of the material (UO_2F_2) and the rate corrected for enrichment (isotopics) via,

$$r_{Ecorr} = r - \left(\frac{nSA_{235}}{nSA_{234}} \cdot m_{235} + \frac{nSA_{238} + \frac{nSFY_{238}}{1.11}}{nSA_{234}} \cdot m_{238} \right) \cdot nSA_{234} \cdot \epsilon_{\alpha,n} \quad \text{Eq. 5}$$

Where r_{Ecorr} is the enrichment corrected rate,

$$r_{Ecorr} = \omega_{234} \cdot m_{234} \quad \text{Eq. 6}$$

The basic process is to measure i mass loadings representative of the material type (UO_2F_2) and enrichment process and gradients for a particular cell. This sets up the systems of equations,

$$r_i = \left(m_{234_i} + \frac{nSA_{235}}{nSA_{234}} \cdot m_{235_i} + \frac{nSA_{238} + \frac{nSFY_{238}}{1.11}}{nSA_{234}} \cdot m_{238_i} \right) \cdot \omega_{234} \quad \text{Eq. 7}$$

These system of equations are solved in a weighted least squares fashion where the weighting is determined by the variance of the background corrected rates,

$$\chi^2(\omega_{234}) = \sum_{i=1}^{M} \frac{\left[r_i - \left(m_{234_i} + \frac{nSA_{235}}{nSA_{234}} \cdot m_{235_i} + \frac{nSA_{238} + \frac{nSFY_{238}}{1.11}}{nSA_{234}} \cdot m_{238_i} \right) \cdot \omega_{234} \right]^2}{\sigma_{r_i}^2} \quad \text{Eq. 8}$$

Where χ^2 is minimized with respect to ω_{234}.

Care must be taken in using the correct nSA_{23x}, "wet" or "dry", or somewhere in between, which may have to be cross-calibrated at another, appropriate, facility.

U-235 Mass Assay

For assays in interfering matrix elements, *e.g.*, DAW (Dry Active Waste), the observed neutron rates are background (environmental) and matrix corrected. This produces the measurement corrected rates, r. To compute the U-234 mass, the rate, r, needs to be corrected for U-235 and U-238; specifically, just as in the case of calibration, the matrix corrected rate must be corrected for U-23x $^{19}F(\alpha,n)^{22}Na$ as well as for spontaneous fission of U-238, *i.e.*,

$$m_{234} = \frac{r}{\omega_{234}} - \left(\frac{nSA_{235}}{nSA_{234}} \cdot m_{235_\gamma} + \frac{nSA_{238} + \frac{nSFY_{238}}{1.11}}{nSA_{234}} \cdot m_{238_\gamma} \right) \quad \text{Eq. 9}$$

Where m_{235_γ} and m_{238_γ} are the measured U-235 and U-238 masses, respectively, from the gamma modality.

Using the "wet" nSA results from Table II and the U-238 SF nSA from Table I we can compute the U-234 mass,

$$m_{234} = \frac{r}{\omega_{234}} - \left(2.00 \cdot 10^{-4} \cdot m_{235_\gamma} + \left(2.14 \cdot 10^{-5} + \frac{7.87 \cdot 10^{-5}}{1.11} \right) \cdot m_{238_\gamma} \right) \quad \text{Eq. 10}$$

To compute the U-235 mass from the U-234 mass, which is the desired goal, a suitable U-235/U-234 gradient is utilized from the AK (Acceptable Knowledge). If no AK is available and the gamma modality is available, and since the gamma modality cannot produce the U-235/U-234 ratio with a reasonable uncertainty, then a site specific correlation is required of the form,

$$m_{235} = m_{234} \cdot \sum_{i=0}^{5} a_i \cdot \left(\frac{m_{238_\gamma}}{m_{235_\gamma}} \right)^i \quad \text{Eq. 11}$$

Where $\frac{m_{238_\gamma}}{m_{235_\gamma}}$ is the ratio of the measured U-238 mass to measured U-235 mass obtained from the gamma modality. The ratio can be determined via measured

isotopics or direct quantification of U-235 and U-238. The a_i coefficients in Eq. 11 are correlation parameters determined from the site specific gradients and can often be time and cell dependent.

At the Portsmouth facility the correlation was calibrated using well established U-235/U-234 and U-238/U-235 gradients supplied by Portsmouth. Similar gradients are developed at the Paducah Gaseous Diffusion Plant.

Results

The B-25 Box Monitor was calibrated for U-234 mass where the rates are corrected for enrichment, environmental background, neutron moderator and high-Z (nuclear spallation) effects from within the matrix.

Uranium Mass

The U-234 mass as a function of net neutron cps and was determined by measuring various loadings of the PPPO-WRM standards (6, 8, 10, 12, 16 and 24), as depicted in Table III. The background corrected rates were further corrected for U-235, U-238 α-n and U-238 spontaneous fission using the specific activities and spontaneous fission yields shown in Table I and Table II. The resultant mass calibration is shown in Fig. 2 where a slope of 0.6453 cps/g U-234 mass ± 1.77% was determined. This calibration is intended to represent the enrichment range 2% to 20% where PORTS has a qualified chart of the U-235/U-234 ratio for this enrichment range as defined in Eq. 11.

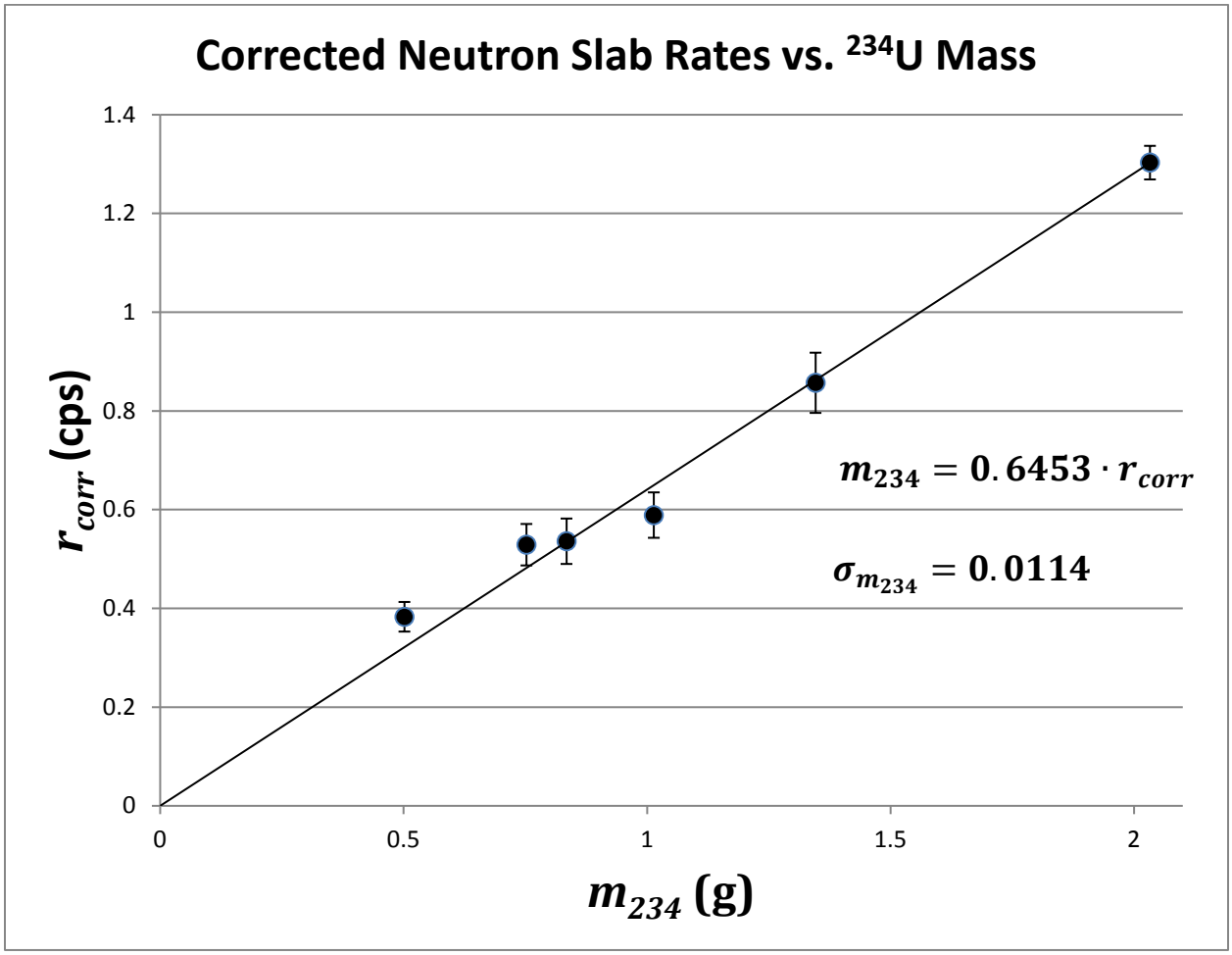

Fig. 2. Mass loading of PPPO WRM standards (5% enrichment) within the empty (QC) box.

Table III PPPO-WRM neutron mass calibration loading configurations

Configuration	PPPO-WRM Standards	U-234 Mass (g)
6	WRM x 6 (08, 09, 14, 17, 35, 38)	0.496
8	WRM x 8 (02, 08, 14, 17, 18, 20, 26, 38)	0.661
10	WRM x 10 (02, 08, 09, 14, 17, 18, 20, 26, 35, 38)	0.827
12	WRM x 12 (08, 11, 12, 13, 17, 18, 21, 24, 25, 29, 30, 34)	0.993
16	WRM x 16 (02, 05, 08, 09, 13, 14, 17, 18, 20, 21, 24, 26, 28, 35, 36, 38)	1.323
24	WRM x 24 (02, 05, 08, 09, 11, 12, 13, 14, 17, 18, 20, 21, 24, 25, 26, 28, 29, 30, 32, 33, 34, 35, 36, 38)	1.985

High-Z Mass

A metals box, just under 2000 kg loaded with scrap steel, was assayed several times and the contribution to the observed neutron rate in the neutron slabs, due to cosmic induced spallation, was determined to be 1.28E-04 cps/kg Fe with an uncertainty of ± 8.24% as shown in Fig. 3. This amount must be subtracted based off the Fe fraction, determined from AK (Acceptable Knowledge) on the B-25 box sample net weight in addition to the normal environmental background.

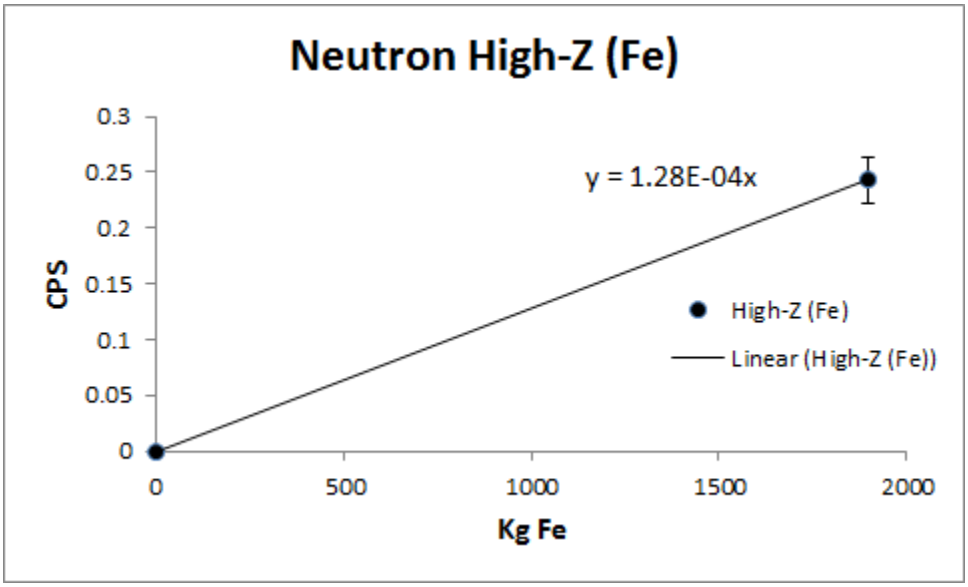

Fig. 3. Calibration of cosmic induced spallation as a function of Fe mass within the B-25 box.

Matrix Correction

The neutron matrix correction (CF) was performed by utilizing 12 and 24 PPPO-WRM volume average configurations within simulated DAW (Dry Active Waste) arrangements, ranging from 0.09-0.55 g/cc and referencing to the corresponding measurements to the empty (0 g/cc) B-25 box. A weighted average response for the matrix correction factor, CF, was generated and is shown in Fig. 4 where a theoretical model was utilized to extend the matrix response to higher-order densities (1.0 g/cc). The volume perturbation calibration was determined to be,

$$Matrix\ \ Correction = \ \ CF = 2.255 \cdot \rho^2 + 1.738 \cdot \rho \qquad \text{Eq. 12}$$

where ρ is the neutron (DAW) moderating matrix (non-metals) density contained within the B-25 box. The uncertainty in the model is assigned to zero where the Total Measurement Uncertainty (TMU) contains a budget to propagate the error associated with this component.

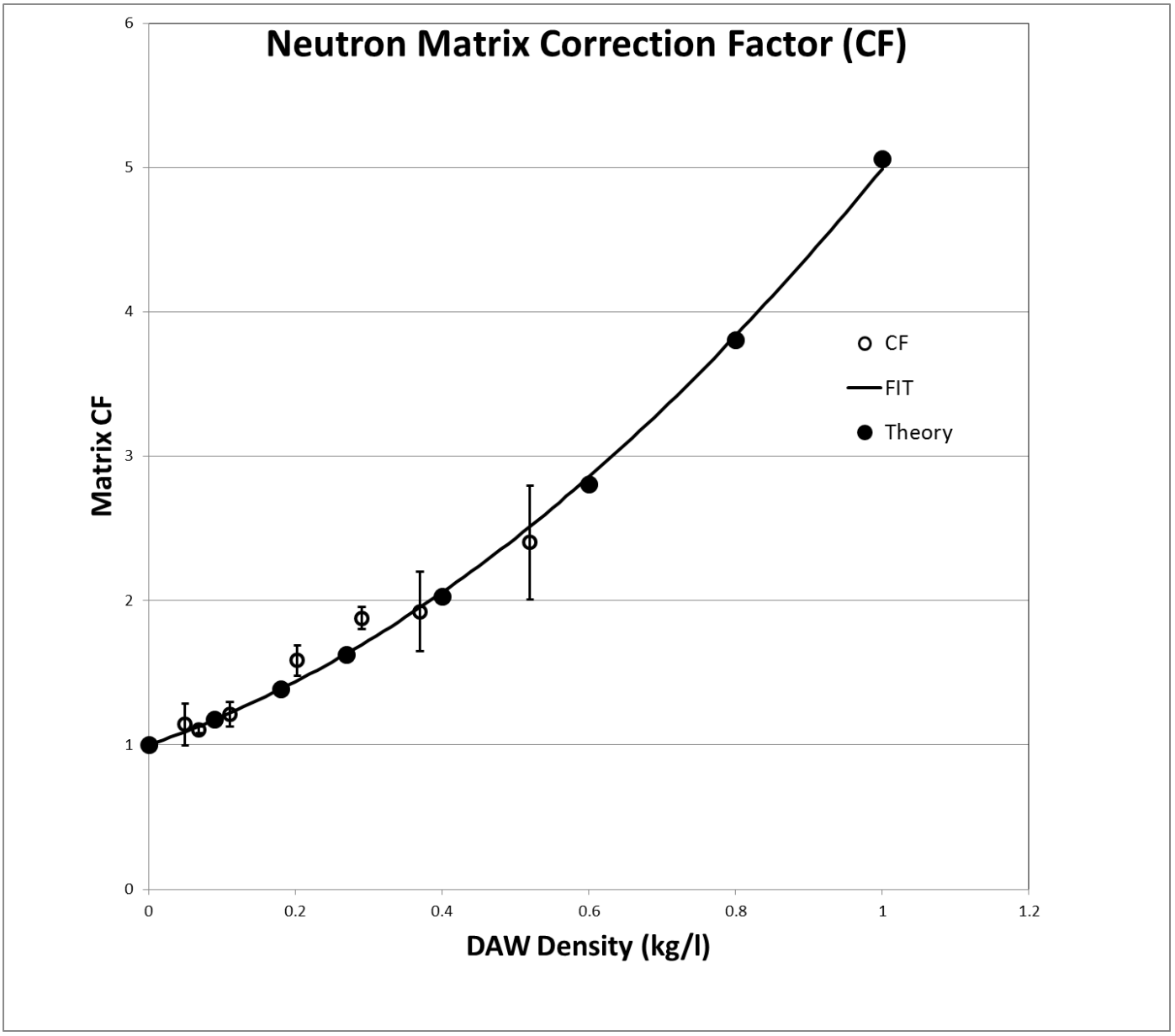

Fig. 4. Measured neutron matrix correction factor and theoretical model for the DAW (cellulose) waste stream in the DAW region.

Background Reduction

The neutron background is also moderated by the hydrogenous content contained within the B-25 box. The general format for the matrix corrected singles rates, R_{corr}, for a given assay is defined as,

$$R_{corr} = CF \cdot (R - CF^{Z} \cdot R_{EC}) \quad \text{Eq. 13}$$

Where *CF* is the neutron matrix correction factor, *R* is the measured assay singles rate, R_{EC} is the measured background singles rate with the empty container (EC) and *Z* is the background reduction parameter to be determined for the system.

To establish the background reduction parameter, a B-25 box was utilized with simulated DAW (Dry Active Waste) materials ranging in density of 0.09 to 0.55 g/cc with no special nuclear material or radioactive nuclides present. The empty B-25 container (EC) was measured followed by a series of measurements of ranging densities and followed once again with the EC so as to bracket. The ratio of the singles rates for the EC (R_{EC}) to the DAW box assay (*R*) was determined for the DAW desnity range. The resulting ratios were fit as a power function of the moderator correction factor (*CF*), as shown in Fig. 5, and the neutron background reduction parameter, *Z,* was determined to be,

$$Z = -0.321 \pm 0.065 \quad \text{Eq. 14}$$

Metals Correction

If the metals fraction of the box net weight is known, then the high-z component can be subtracted from the matrix corrected, $R_{corr,}$ rates using,

$$R_{metals} = R_{corr} - CF_{M}^{Z+1} \cdot M \cdot f_{metals} \cdot a \quad \text{Eq. 15}$$

Where R_{metals} is the corrected rate, *M* is the net weight of the box, f_{metals} is the estimated fraction of the net weight that is metals and the parameter, *a* , is the metals calibration parameter (*a* = 1.28e-04 cps/Kg Fe) shown in Fig. 3. The matrix correction factor is calculated using a reduced DAW (Dry Active Waste) density, ρ,

$$\begin{aligned} Metals\ \ Matrix\ \ Correction = \ \ & CF_{M} \\ & = 2.255 \cdot \left((1 - f_{metals}) \cdot \rho\right)^{2} + 1.738 \cdot (1 - f_{metals}) \cdot \rho \end{aligned} \quad \text{Eq. 16}$$

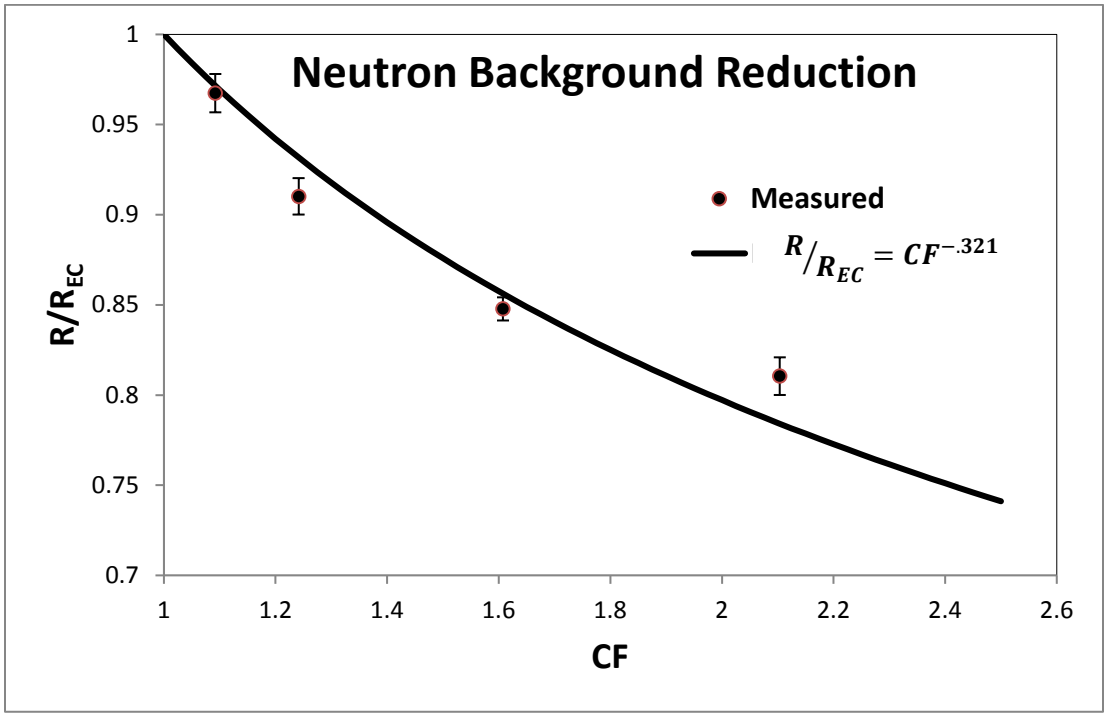

Fig. 5. Calibration of the neutron background reduction parameter.

Discussion

The mass calibration method requires that the UO_2F_2 WRM's (Working Reference Materials) be cross calibrated for nSA as described in [3]. The nSA of the unknown waste matrix is, of course, not known and the nSA of the WRM's average is then taken. The variance in the nSA then leads to a Total Measurement Uncertainty (TMU) budget which may be rather substantial. In general it is best to assume the "wet" nSA which leads to a more conservative result.

Care must be taken to mitigate biases in the neutron rates due to fluctuations in the environmental background. It is highly recommended that the environmental background be performed prior to, and upon completion, of the daily batch. The counting statistics and count time of the environmental background must be adjusted such that the target Minimal Detectable Activities (MDA) can be achieved.

Since the U-235/U-234 and U-238/U-235 gradients can wildly fluctuate with enrichment range or the gradients can be cell or time dependent, it is suggested that there be provisions for input of multiple gradient parameterizations as described by Eq. 11.

CONCLUSION

The methods described in this paper describe the technique for exploiting the

measured neutron signal from the 19F(α, n)22Na reaction, from selected Uranium α-emitters, in UO_2F_2-bearing materials to obtain a measured U-235 mass. The methods include a calibration technique which produces a calibration parameter as a function of U-234 mass using Working Reference Materials (WRM's) with appropriate isotopics. The methods also include a means for quantifying U-235 mass using the matrix corrected neutron rates in conjunction to the measured gamma results (quantitative gamma and/or isotopics).

REFERENCES

[1] Passive Non-Destructive Assay (PANDA) Manual, Los Alamos Publication LA-UR-90-732, March, 1991.

[2] Mayer II, R.L., Litteral, J.D., Banks, K.D., Montgomery, J.B., Lanning, B.M., Lynch, B.P., 2008, *Neutron Specific Activity of uranium Isotopes in UO_2F_2*, Proceedings of the 49th Annual Meeting of the Institute of Nuclear Materials and Management (INMM), Nashville, TN.

[3] LaFleur, A.M., Croft , S., Mayer, R.L., Swinhoe, M.T. , Mayo, D.R., Sapp, B.A., 2013, *Traceable Determination of the Absolute Neutron Emission Yields of UO_2F_2 Working Reference Materials*, LA-UR-13-23768, No. 1093, Proceedings of the 2013 3rd International Conference on Advancements in Nuclear Instrumentation, Measurement Methods and their Applications (ANIMMA), Marseille, France.