Guide for Employing High-Resolution Gamma Spectroscopy for ^{252}Cf Source Age and Isotopic Composition

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Abstract

Californium-252 is commonly used as a calibration source for neutron coincidence and neutron multiplicity counting in nuclear safeguards. Accurate knowledge of the neutron emission rate, age, and isotopics of the source (i.e., "source term") are important for ensuring the best possible accuracies in item assay results. Californium-252 sources are not usually measured using gamma spectrometry, because of the assumption that their gamma-ray spectra appear to provide little information. However, gamma-ray signatures produced from ^{252}Cf spontaneous fission products and odd-numbered Cf isotopes can be useful in determining source age and Cf isotopic composition. We demonstrate the utility of high-resolution gamma spectrometry in determining the age and isotopics of Cf neutron sources. In this work, five ^{252}Cf sources were measured using a high-purity germanium detector. The neutron flux was small enough that radiation damage from prolonged neutron exposure was not substantial. Spectra were collected in 2-hour increments for 42–48 hours for quality control. The 2-hour spectra were added together to create a single spectrum for each source, and peak analyses were performed. Source ages were determined using a method that involved experimentally measuring the ratio of the gamma-ray emission rate of the 661.657 keV from ^{137}Cs relative to a short-lived fission product and exploiting the dependence of this ratio on the source age. Source age was solved for using emission rates from four different gamma lines from four short-lived spontaneous fission products. Analysis results from all four fission products returned statistically similar source ages, but two had uncertainties greater than 25% because of high spontaneous fission product yield uncertainties as nominally high as 63%. Choosing short-lived fission products with small yield uncertainties is most important for accurately calculating source age. Additionally, the calculated ages did not always match the time since ^{248}Cm separation well, which is often assumed to be the source age on the technical data sheet provided by the manufacturer. Activity ratios of ^{249}Cf to ^{251}Cf, the only Cf gamma emitters present in a ^{252}Cf source, also did not match between experimental data and data on the technical data sheet provided by the vendor. It is thus recommended that newly purchased Cf sources be examined using gamma spectrometry to determine the source age and confirm isotopic composition of a ^{252}Cf calibration source.

I. Introduction

Californium-252 ($T_{1/2}$ = 2.645 y [1]) is a common neutron calibration source for neutron coincidence and multiplicity counting in nuclear safeguards. This isotope has a high spontaneous fission yield (3.09%), a high neutron emission rate per unit mass ($2.31 \cdot 10^6$ s^{-1} μg^{-1}), and a prompt fission spectrum similar to other important neutron emitters in the fuel cycle, namely ^{240}Pu [1,2]. Californium-252 is also the dominant neutron emitter in chemically separated Cf, so a fresh source resembles a pure ^{252}Cf emitter. Consequently, ^{252}Cf is a convenient isotope to

make compact neutron sources that approximate a point source for calibrating nuclear safeguards instruments.

Gamma-ray spectroscopy is rarely performed on ^{252}Cf sources intended for metrological purposes because the gamma-ray spectra have generally been assumed to provide little useful information. However, gamma-ray signatures from spontaneous fission products (SFPs) appear in the spectrum and have been exploited to estimate ^{252}Cf source age [3]. Source ages can be calculated by setting the experimental ratio of the gamma-ray emission rate from the 661.657 keV line from ^{137}Cs ($T_{1/2}$ = 30.08 y [4]) to the gamma-ray emission rate from a short-lived fission product equal to the theoretical ratio of the same gamma-ray emission rates derived using the Bateman equations and solved for time. In essence, ^{137}Cs logs the total number of fissions, whereas the shorter-lived nuclides mark present decay rates. Previous work has measured source age to within 1% of the source age reported by the vendor [3]. The previous work did not, however, include measurement uncertainty or fission product grow-in from secondary neutron emitters in the model.

The present work used high-resolution gamma-ray spectroscopy to confirm source age and isotopic ratios present in ^{252}Cf sources. Uncertainty analyses were also performed to determine which short-lived product(s) are the best candidates for calculating source age using gamma-ray spectroscopy.

II. Spectrum Collection

Gamma-ray spectra were collected using an n-type high-purity germanium detector (Model GL2820 R/S, Canberra Industries, Meriden, Connecticut). The primary concern about collecting a gamma-ray spectrum from a ^{252}Cf source was radiation damage to the detector from prolonged neutron exposure. The neutron flux from each neutron source was determined to be small enough to not cause substantial radiation damage. However, as a precaution to prevent damage from prolonged neutron exposure, an aged detector with degraded performance was used after preliminary results established that the spectral quality was acceptable. Full-width-at-half-maximum (FWHM) was 1.67 keV at 122 keV and 3.08 keV at 1408 keV.

Energy calibration and detection efficiency were determined using a ^{152}Eu point source (4.7 μCi) to establish the detector response from a wide range of gamma-ray energies. The source was placed 15 cm along the centerline of the detector. A 2-hour gamma-ray spectrum and 2-hour background spectrum were collected. The background spectrum was subtracted from the ^{152}Eu spectrum using PeakEasy 4.98.1 [5]. Peak locate and peak analysis algorithms in Genie 2000 Spectroscopy Software [6] were used to locate ^{152}Eu peaks and quantify the net count rate and associated uncertainty for each peak. The absolute full-peak detection efficiency curve was constructed using the seven most probable and isolated gamma rays in the ^{152}Eu spectrum. The absolute full-energy peak efficiency, ϵ_{abs}, was calculated for each peak by

$$\epsilon_{abs} = \frac{CR}{A \cdot I_\gamma} \quad (1)$$

where *CR* is the net count rate in the full-energy peak, *A* is the decay-corrected source activity, and $I\gamma$ is the gamma-ray yield. A power fit was applied to the seven data points to create an

absolute detection efficiency curve. An R-squared analysis, R^2, was performed to measure how well the power fit matched the data. An $R^2 = 1$ indicates an excellent fit to the data, and an $R^2 = 0$ indicates a poor fit to the data. The power fit had an $R^2 = 0.996$, indicating an excellent fit to the data. The power fit was then normalized to the absolute efficiency value at 661.657 keV to create the relative detection efficiency curve, $\epsilon_{rel}(E)$. Note that the relative efficiency curve is applicable for sources placed at varying distances with no added absorbers between the source and detector. The detector response of one gamma-ray energy relative to a second gamma-ray energy will remain constant with changing distance; only the source intensity changes with distance. The attenuation in the ^{152}Eu source is negligible over the energy range of interest and approximately cancels when the relative efficiency curve is formed.

Five ^{252}Cf sources were measured. It is highly likely that all source material can be traced to Cf produced in the High Flux Isotope Reactor at Oak Ridge National Laboratory. Spectra and background were collected in 2-hour increments for a total duration of 42–48 hours. The 2-hour spectra were collected for quality control.. Sources 1–4 were placed 15 cm from the face of the detector along the centerline and source 5 was placed 20 cm from the face of the detector along the centerline. These distances were chosen to reduce the deadline under 10% and minimize true coincidence summing. Each 2-hour spectrum was summed for each source and background subtracted in PeakEasy 4.98.1 [5]. Each spectrum was normalized to the maximum count rate within the 661.657 keV peak from ^{137}Cs for comparison. The resulting spectra are shown in Fig. 1. From left to right, the prominent peaks in order of increasing energy are curium K-series x-rays between 104 and 123 keV, ^{251}Cf gamma-ray peak at 177.52 keV, ^{249}Cf gamma-ray peaks at 333.37 and 388.17 keV, and ^{137}Cs gamma-ray peak at 661.657 keV. All other discernable peaks are short-lived spontaneous fission products.

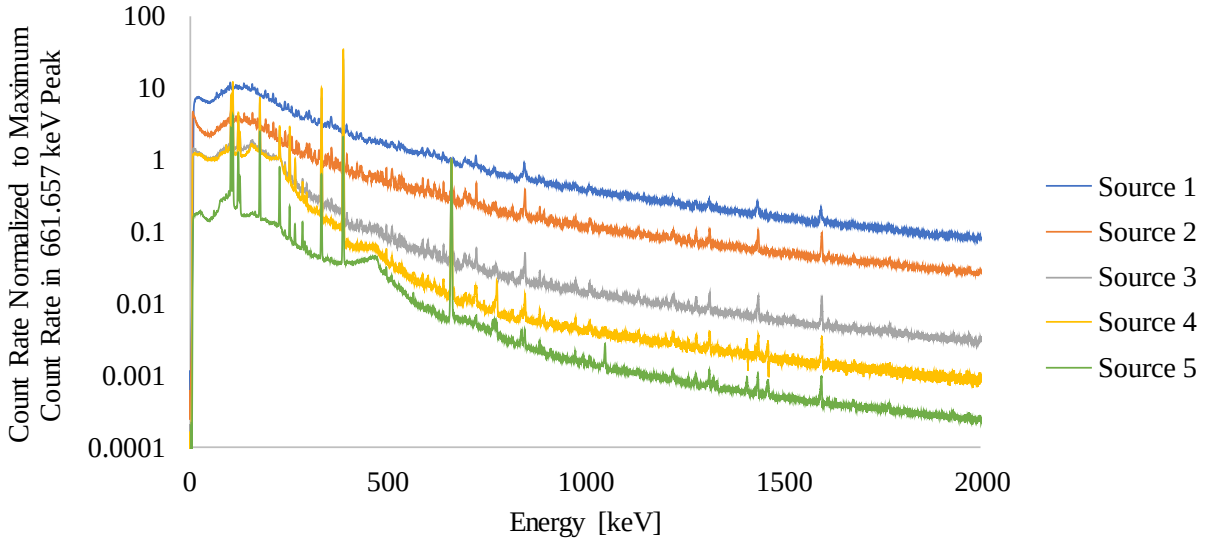

Fig. 1 Californium-252 spectra for sources 1–5 normalized to the maximum count rate in the 661.657 keV gamma-ray peak from ^{137}Cs

III. Californium-252 Source Age Calculation and Uncertainty Analysis

1. Methodology

Source ages were calculated by setting the experimental ratio of gamma-ray emission rates from two SFPs, ^{137}Cs and a short-lived SFP isotope *x*, equal to the theoretical ratio of the same gamma-ray emission rates derived using the Bateman equations. Time, present in the theoretical ratio from the Bateman equations, is solved to determine source age. Time in this case represents time passed since the last curium separation and not time since production batch irradiation, because the fission products would have been stripped from the source during the curium separation.

The experimental gamma emission rate ratio, R_{exp}, was calculated using the count rate from each gamma-ray peak and accounting for relative detection efficiency such that

$$R_{exp} = \frac{CR_{Cs137}}{CR_x} \cdot \epsilon_{rel,661}(E_{\gamma,x}) \tag{2}$$

where CR_{Cs137} and CR_x are the count rates in the full energy peaks associated with gamma-ray emission from ^{137}Cs and isotope *x*, respectively. These values were determined using peak locate and peak analysis algorithms in Genie 2000 Spectroscopy Software [6], which located fission product peaks and quantified the net count rate and associated uncertainty for each identified peak in the spectrum.

The theoretical ratio required deriving the gamma-ray emission rates from the Bateman equations. SFP in-growth into a ^{252}Cf source was assumed to only result from decay of ^{252}Cf; SFP in-growth from secondary neutron emitters was assumed to be negligible. An initial ^{252}Cf activity, $A_{0,Cf252}$, was assumed to be present at time $t = 0$, and the SFP initial activity was assumed to be zero. The resulting gamma-ray emission rate equation, $G_x(t)$, for in-growth of SFP *x* in a ^{252}Cf source under these assumptions was

$$G_x(t) = \frac{\lambda_x}{\lambda_x - \lambda_{Cf252}} \cdot S_{Cf252} \cdot Y_{x,Cf252} \cdot I_x \cdot A_{0,Cf252} \cdot \left(e^{-\lambda_{Cf252}t} - e^{-\lambda_x t}\right) \tag{3}$$

where λ_{Cf252} is the overall decay constant accounting for alpha decay and spontaneous fission of ^{252}Cf [y^{-1}], λ_x is the decay constant of SFP *x* [y^{-1}], S_{Cf252} is the ^{252}Cf spontaneous fission rate [fissions/decay], and $Y_{x,Cf252}$ is the cumulative SFP yield of isotope *x* from ^{252}Cf [atoms of isotope *x*/fission], and I_x is the gamma-ray yield [gammas/decay]. The theoretical ratio was then calculated to be

$$R_{th} = \frac{G_{Cs137}(t)}{G_x(t)} \tag{4}$$

where $G_{Cs137}(t)$ is the gamma-ray emission rate of ^{137}Cs.

Source age, *t*, was solved numerically by setting Eqn. 2 equal to Eqn. 4 such that

$$\frac{CR_{Cs137}}{CR_x} \cdot \epsilon_{rel,661}(E_{\gamma,x}) = \frac{\frac{\lambda_{Cs137}}{\lambda_{Cs137} - \lambda_{Cf252}} \cdot Y_{Cs137,Cf252} \cdot I_{Cs137} \cdot \left(e^{-\lambda_{Cf252}t} - e^{-\lambda_{Cs137}t}\right)}{\frac{\lambda_x}{\lambda_x - \lambda_{Cf252}} \cdot Y_{x,Cf252} \cdot I_x \cdot \left(e^{-\lambda_{Cf252}t} - e^{-\lambda_x t}\right)} \quad (5)$$

Uncertainty analysis associated with this calculation is described in the following section.

2. Uncertainty Analysis

The standard deviation for source age, σ_t, was calculated using

$$\sigma_t^2 = \sum_{n=1}^{10} \sigma_u^2 \left(\frac{\partial u}{\partial t}\right)^2 \quad (6)$$

where *u* is a dummy variable that was substituted with each of the ten variables in Eqn. 5. The derivative in Eqn. 6 could not be analytically derived from Eqn. 5, because *t* could not be isolated. Instead, a numerical approximation was used to estimate the derivative.

The numerical approximation was estimated as the slope of a line passing through *t* for each variable included in Eqn. 6. The change in *t* due to change in *u* was approximated as

$$\frac{\partial u}{\partial t} = \frac{t(u + \sigma_u) - t(u - \sigma_u)}{2\sigma_u} \quad (7)$$

where σ_u is the uncertainty of the dummy variable *u*. The dummy variables in Eqn. 7 were substituted for the value and uncertainty associated with each variable in Eqn. 5. This was repeated for each variable included to solve for the uncertainty of source age in Eqn. 6.

3. Short-lived Spontaneous Fission Products

Four short-lived SFPs were chosen to calculate source age of the five ^{252}Cf sources. These isotopes and their properties are listed in Table 1. No uncertainty was provided for three gamma-ray yields, so the associated uncertainty was assumed to be zero. Two isomers contributed to the overall gamma-ray emission rate for ^{136}I; fission product yields of the metastable isomer for all other isotopes were less than 1% of the fission product yield for the ground isomer and were assumed to be negligible. The model was modified to account for this phenomenon by using Eqn. 3 to calculate the gamma-ray emission rate contribution from each isomer. The contribution from each isomer was added together to produce the total gamma-ray emission rate, which is represented by $G_x(t)$ in the denominator of Eqn. 4.

Table 1. Properties of ^{252}Cf spontaneous fission product properties used to calculate source age in an unknown ^{252}Cf source. Uncertainties are in parentheses.

Isotope	Energy [keV]	Half-Life	Gamma-ray Yield [gamma/decay]	Fission Product Yield [atoms/fission] [11]
^{137}Cs [4]	661.657(3)	30.08(9) y	0.851(2)	0.0502(20)
^{132}I [7]	667.714(2)	2.295(13) h	0.987*	0.0215(137)
^{136}I [8]	1313.02(10)	83.4(4) s	0.667*	0.0228(53)
^{136m}I [8]	1313.02(10)	46.6(10) s	1.00*	0.00939(42)
^{138}Cs [9]	1435.77(7)	32.5(2) min	0.763(5)	0.0547(15)
^{140}La [10]	1596.21(4)	1.67855(12) d	0.9540(8)	0.0596(8)

*No uncertainty provided

Calculated source ages and associated uncertainties are listed in Table 2 for each spontaneous fission product and the average age from all spontaneous fission products. The average source age represents the weighted average source age and associated weighted uncertainty. All individual spontaneous fission product source ages were within 2-σ of each other for each source. The agreement among different SFPs indicates that this is a robust method for calculating source age of a ^{252}Cf source.

Sources 3–5 have a calculated source age old enough such that ^{250}Cf ($T_{1/2}$ = 13.08 y), a secondary neutron emitter present in all ^{252}Cf sources with a spontaneous fission rate of 0.077%, contributes more than 10% to the neutron emission rate [12,13]. This statement is based on the observation that the ^{250}Cf to ^{252}Cf mass ratio is at least 10%. The assumption that SFP in-growth stems only from ^{252}Cf is no longer valid for these sources, and the model is no longer applicable without modification. A second model has been developed to account for secondary neutron emitters and will be reported elsewhere. However, general conclusions are not strongly affected.

Table 2. Calculated sources ages of ^{252}Cf sources with associated uncertainty.

Isotope	Source Age [y]				
	1	2	3	4	5
^{136}I	12.2±0.9	14.5±0.9	24.2±1.0	29.6±1.0	33.0±1.0
^{138}Cs	14.7±0.3	16.2±0.2	25.8±0.2	31.6±0.3	35.1±0.2
^{140}La	14.4±0.5	16.1±0.3	25.7±0.2	31.6±0.3	35.1±0.3
^{132}I	11.8±2.9	14.6±3.1	24.3±3.2	28.6±3.2	33.1±3.2
Average	14.4±0.3	16.1±0.2	25.7±0.2	31.5±0.2	35.0±0.2

The individual source age values in Table 2 demonstrate that certain SFPs result insource age measurements with less uncertainty than others. Iodine-132 and ^{136}I have larger uncertainties associated with their measurements than ^{138}Cs and ^{140}La in all cases. This is a direct result of large uncertainties associated with the spontaneous fission product yield for these two isotopes. As shown in Table 1, ^{132}I and ^{136}I have SFP yield uncertainties of 64% and 23%, respectively. These uncertainties ultimately drive the quality of the final source age uncertainties. Quality nuclear data is essential for obtaining a source age measurement with low uncertainty. The limiting variable in these cases was SFP yields, but it could be other variables for different isotopes. Care should be taken when choosing SFPs for calculating ^{252}Cf source age.

4. Comparison of Calculated and Reported Source Ages

Source ages were compared between experimental data and the value reported on the technical data sheet (TDS), and the results are displayed in Fig. 2. A TDS was not available for sources 4 and 5, so it was not possible to compare experimental and reported source ages. Source 2 has the only calculated source age within 1-σ of the reported source age; sources 1 and 3 were statistically different at 3-σ.

One possibility to explain this discrepancy is excess ^{137}Cs present in the source as an impurity or contaminant. However, radiochemical processing readily separates alkali metals, such as Cs, from actinides, such as Cf, during the ion exchange process, making it unlikely for ^{137}Cs to be present as an impurity. Additionally, these facilities are routinely monitored for contamination in the work area, making it also unlikely that a source left the facility contaminated with ^{137}Cs. Ultimately, no means were identified for excess ^{137}Cs to be present as an impurity or contaminant in the source.

The second possibility is that vendors did not send the correct technical data sheet along with the source when it was purchased. This possibility will be discussed in further detail in the following section.

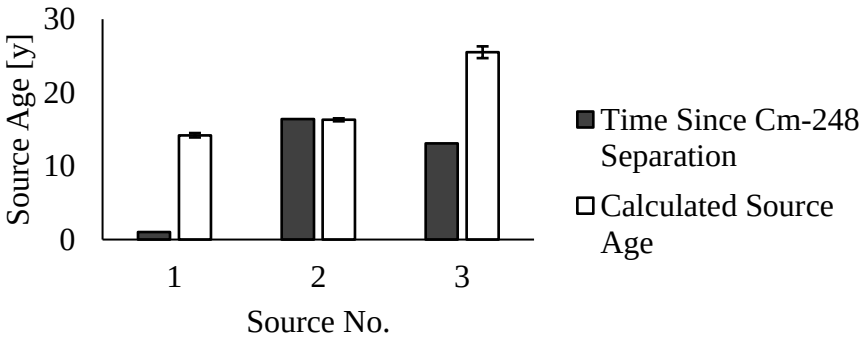

Fig. 2 Comparison of source ages from reported date of ^{248}Cm separation on the technical data sheet to the calculated source age. Error bars on the experimental data are ±1σ.

IV. Isotopic Ratio Verification

Californium-250 and ^{252}Cf do not emit gamma rays and thus cannot be directly measured via gamma-ray spectroscopy to confirm their isotopic composition in a source. However, isotopic analyses on the TDS provide information about the $^{249–254}$Cf isotopes relative to each other. Highly probable gamma rays emitted from the decay of long-lived, odd-numbered Cf isotopes, ^{249}Cf and ^{251}Cf, can be exploited to verify isotopic information provided on the TDS for all Cf isotopes, including ^{252}Cf and ^{250}Cf.

The 388 keV gamma ray from ^{249}Cf and 177 keV gamma ray from ^{251}Cf were used to compare the ratio of ^{249}Cf to ^{251}Cf from experimental data to values provided on the technical data sheet. The experimental isotopic ratio, R_{iso}, was calculated by

$$R_{iso} = \frac{CR_{Cf249}(388\ keV) \cdot \epsilon_{rel}(177\ keV) \cdot I_{Cf251}}{CR_{Cf251}(177\ keV) \cdot \epsilon_{rel}(388\ keV) \cdot I_{Cf249}} \quad (8)$$

where $CR_{Cf249}(388\ keV)$ and $CR_{Cf251}(177\ keV)$ are the count rates in the 388 keV peak from ^{249}Cf and the 177 keV peak from ^{251}Cf, respectively, and I_{Cf249} and I_{Cf251} are the gamma-ray yields of the respective peaks emitted by each isotope. The TDS ratio was obtained by dividing the isotopic value of ^{249}Cf to the isotopic value of ^{251}Cf listed on the data sheet. These values were decay corrected from the isotopic analysis date to the measurement date, but the correction was negligible as both isotopes have long half-lives.

Figure 3 displays the ^{249}Cf/^{251}Cf ratios calculated from experimental data and TDS values. For source 2 only, the experimental ^{249}Cf/^{251}Cf ratio agrees with the isotopic ratio reported on the TDS at 1-σ; sources 1 and 3 were statistically different at 3-σ. However, no pathway exists, other than radioactive decay, for the quantity of these isotopes to change from the initial reported quantity. In-growth of these isotopes is not possible, because they can only be created from successive neutron captures of Cm and Bk, which are stripped from the source after irradiation. Thus, the experimental ratio of these two isotopes should match the TDS ratio. The fact that these ratios do not match for two of the three sources considered here could be an indication that the TDS provided by the vendor does not match the source characteristics. Coupled with large discrepancies in the calculated and reported source ages leads to the conclusion that the TDS provided by the vendor do not belong to the sources purchased.

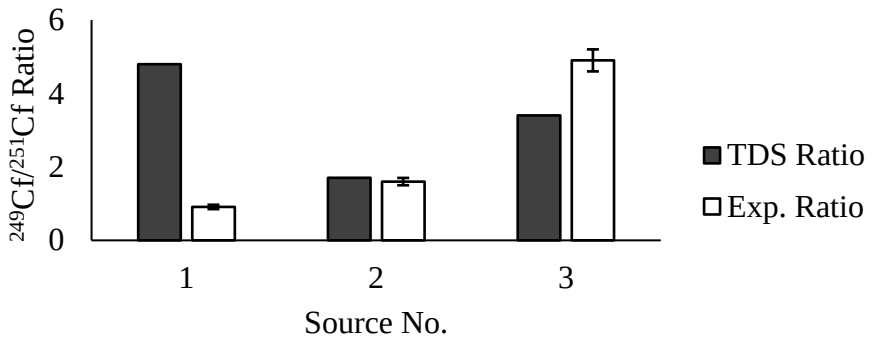

Fig. 3 Comparison of ^{249}Cf/^{251}Cf ratios from TDS values to experimental data. Error bars on the experimental data are ±1σ.

V. Conclusions

The present work demonstrated the utility of performing gamma spectroscopy on ^{252}Cf source to verify source age and isotopic ratios. Age and isotopic data are needed to make accurate decay corrections inclusive of the ^{250}Cf contribution to the neutron yield. High-resolution gamma-ray spectroscopy can be employed to confirm or query the content of a ^{252}Cf neutron calibration source as reported from the vendor-supplied TDS. Analysis results from all four SFPs used for calculating source age returned statistically similar source ages despite large nominal uncertainties associated with properties of two of the SFPs. Source age and isotopic ratio experimental data for source 2 were within 1-σ of the values reported on the TDS, demonstrating that this method has the potential to produce accurate results. However, sources 1 and 3 were shown to have statistically different source age and isotopic ratio values at 3-σ. This suggested that an impurity or contamination was present in the source. After exhausting all other

possibilities to explain the discrepancies, it was concluded that an incorrect TDS was most likely provided for these sources.

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References
[1] M. J. Martin, Nuclear Data Sheets for A = 248, Nuclear Data Sheets, 122 (2014) 377–409.
[2] D. Reilly, N. Ensslin, H. Smith Jr., S. Kreiner, Passive Nondestructive Assay of Nuclear Materials, 1991.
[3] R. J. Gehrke, R. Aryaeinejad, J. K. Hartwell, W. Y. Yoon, E. Reber, J. R. Davidson, The gamma-ray spectrum of ^{252}Cf and the information contained within it, Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms, 213 (2004) 10–21.
[4] E. Browne, J. K. Tuli, Nuclear Data Sheets for A = 137, Nuclear Data Sheets, 104(3) (2005) 497–790.
[5] PeakEasy 4.98.1 [Computer software] (2018). Los Alamos, NM: Los Alamos National Laboratory.
[6] Genie 2000 Spectroscopy Software (V3.4.1) [Computer software] (2016). Meriden, CT: Mirion Technologies (Canberra) Inc.
[7] Y. Khazov, A. Rodionov, S. Sakharov, B. Singh, Nuclear Data Sheets for A = 132, Nuclear Data Sheets, 104(3) (2005) 497–790.
[8] A. Sonzogni, Nuclear Data Sheets for A = 136, Nuclear Data Sheets, 95(4) (2002) 837–994.
[9] J. Chen, Nuclear Data Sheets for A = 138, Nuclear Data Sheets, 146 (2017) 1–386.
[10] N. Nica, Nuclear Data Sheets for A = 140, Nuclear Data Sheets, 108(7) (2007) 1287–1582.
[11] M. B. Chadwick, et al., ENDF/B-VII.1 Nuclear Data for Science and Technology: Cross Sections, Covariances, Fission Product Yields and Decay Data, Nuclear Data Sheets, 112(12) (2011) 2887–2996.
[12] E. Browne, J. K. Tuli, Nuclear Data Sheets for A = 246, Nuclear Data Sheets, 146 (2017) 387–510.
[13] N. Roberts, L. Jones, The content of ^{250}Cf and ^{248}Cm in ^{252}Cf neutron sources and the effect on the neutron emission rate, Radiation Protection Dosimetry, 126(1–4) (2007) 83–88.