

Sources of Bias in Environmental Sample Radioisotope Activity Measurements at USACE FUSRAP Maywood Laboratory -14353

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ABSTRACT

The U.S. Army Corps of Engineers (USACE) Formerly Utilized Site Remedial Action Program (FUSRAP) Maywood Superfund Site has an onsite laboratory that has been State-certified since 2003 for measurement of various radionuclide activities in water and soil. This paper describes random and systematic measurement bias observed gamma spectroscopy, alpha spectroscopy and gas proportional detector methods employed at the USACE FUSRAP Maywood Laboratory (UFML).

In gamma spectroscopy, various contributions to counting uncertainty and bias such as library yield assignments and standard versus sample density among others have been identified and quantitated. In alpha spectroscopy and gas proportional detector counting systems, sources of measurement bias occur during sample preparation (e.g. sample loss, volume uncertainty, and others) and during counting (e.g. standard versus sample composition, interferences, and others). Specific measurement bias and quantification are discussed in detail.

One of the advantages of having a project-specific onsite laboratory is the opportunity to better understand measurement factors, variables, and anomalies that impact measurement accuracy and precision. Such understanding has lead to more informed decision-making regarding assessment of contaminated media radioisotope activities relative to project-specific action levels at the Maywood project.

The results show that sources of random uncertainty, once identified, may be reduced or eliminated by making specific method modifications. For example, changing the yield values of gamma spectroscopy energy lines to more up-to-date values, or changing the curve fitting algorithm of a gross alpha efficiency curve, can reduce bias.

Sharing information such as the identification and removal or reduction of bias sources with other FUSRAP, DOE and DOD groups involved in remediation of radiologically-contaminated sites should facilitate better decision-making regarding determinations of contaminated vs. uncontaminated media, and allow for more accurate estimates of costs associated with such remedial efforts.

INTRODUCTION

The FUSRAP Maywood Superfund Site (FMSS) is in the latter stages of an extensive remediation of radiologically-contaminated residential and non-residential properties. The former Maywood Chemical Works, which operated from about 1895 to 1959, made a number of chemical products, one of which was thorium nitrate salt, isolated from the naturally-occurring thorium ore called monazite. Some of the monazite ores processed by the Maywood Chemical Works also contained significant levels of uranium. The thorium salt was sold to a cloth company which manufactured gas mantles using the thorium salt. Since disposal practices during that time period were poor or non-existent, the waste from the thorium processing operation were channeled into man-made lagoons, essentially giant ditches, to “contain” the waste. Naturally, over the many ensuing years, stormwater incursions caused transport of the waste,

especially the fine solids, downgradient and much of that waste was transported by the nearby natural surface water flows of Lodi and Westerly Brooks.

Most of the current remedial efforts are centered around two of the larger industrial properties, Sears (SLS) and Stepan Chemical Company, as well as the government-owned Maywood Interim Storage Site (MISS) which has served as the staging area for transport of the waste soils that have been excavated from adjacent vicinity properties. The cleanup criteria are 5 pCi/g above background for residential property soils and 15 pCi/g for non-residential property soils for the sum of the activities of Th-232 and Ra-226, and 50 pCi/g above background for U-238.

The FMSS is somewhat unique in that it has an onsite radiological testing laboratory, which has been certified since 2003 for the testing of soil samples using gamma spectroscopy, and water samples using alpha spectroscopy and gas proportional detector counting systems. Some of the measurement biases associated with radiological methods employing these instruments are discussed below.

DISCUSSION

Bias

Bias can be defined as a measurement deviation, positive or negative, from a true value. Bias is considered “in control” if it is less than two times the standard deviation of the method stated reproducibility (essentially two times the precision; from Guide for Estimation of Measurement Uncertainty in Testing (G104-A2LA July 2002)[1].

Bias is often divided into two categories: systematic and random. Systematic bias is a bias that is quantifiable. Assuming that an analyst or data user is aware of the sources of systematic bias, they can be accounted for by modifying a measured value. One would be concerned if there are significant sources of systematic bias of which the analyst is unaware as this would cause inaccurate reporting of sample results. Sources of random bias are typically more subtle and smaller in magnitude and are not easily quantified. Only systematic bias will be discussed in this paper. A number of potential sources will be described and examples will be provided.

Gamma Spectroscopy

Sources of measurement bias and quantification include coincidence summing, random summing, uncertainties in the slope or shape of the efficiency curve and energy curve, and the accuracy of library energy and yield assignments. In addition, differences between the calibration standard density and sample density, calibration standard activity uncertainty, and uncertainty in soil sample weight contribute to measurement bias.

Coincidence Summing

Coincidence summing occurs in gamma spectroscopy when radionuclides emit two or more photons (so-called gamma cascade) within the resolving time of the spectrometer thus giving rise to signals at energies greater than the energy of interest. The measured activity at the energy of interest is then biased low and must be adjusted using a correction factor C. Co-60 is an example; 1173.2 keV and 1332.5 keV photons are emitted from consecutive excited state decay events and interact with the detector simultaneously, thus giving rise to a sum peak at 2505.7 keV. There are three ways coincidence loss is typically addressed in gamma spectroscopy.

- Count the sample farther away from the detector
- Correct for the loss mathematically and use a correction factor
- Determine the true counting efficiency with the same radionuclide being counted in the sample

At the Maywood project site, Ac-228, a radioisotope daughter of Th-232 that is in secondary equilibrium with Th-232, is measured. Ac-228 has two peaks at 911.2 keV and 969.0 keV that may coincidence sum. For a solid matrix in a Marinelli geometry, Garcia-Talavera calculates a correction factor of 1.05 for the Ac-228 911.2 keV peak (from Coincidence Summing Corrections for the natural decay series in γ -ray spectrometry) [2]. Similarly, Pb-214 has a correction factor of 1.01. These correction factors have been incorporated into the Maywood gamma spectrometer quantitation software. Prior to this correction, Ac-228 would have had a 5% low bias due to coincidence summing.

Random Summing

The random summing count rate is $2A^2t$ where A is the counts per unit time and t is the detector resolving time (MARLAP, Sect. 15.6.3.3). Thus random summing is strongly dependant on the count rate, A . (see 6.11.4 of Gamma Vision manual [3]). The Maywood laboratory employs three gamma spectrometry detectors as follows: Canberra High Purity Germanium (HPGe) 30% efficiency detector (GC3020), Canberra HPGe 40% efficiency detector (GC4020) and Ortec-Ametek HPGe 40% efficiency detector (GEM40). For these detectors, the resolving time is 12 μ s, or 1.2E-05 sec. So, if the sample count rate is 100 counts/min, the summing count rate is 0.24 counts/min, or 0.24% of the sample count rate, and if the sample count rate is 1000 counts/min, the summing count rate is 24 counts/min, or 2.4% of the sample count rate. As the sample count rate increases by a factor of 10, the summing count rate increases by a factor of 100, and thus the percentage contribution of the summing count rate goes up by a factor of 10 with each factor of 10 increase in the sample count rate.

Figure 1 shows simple examples of coincidence summing and random summing.

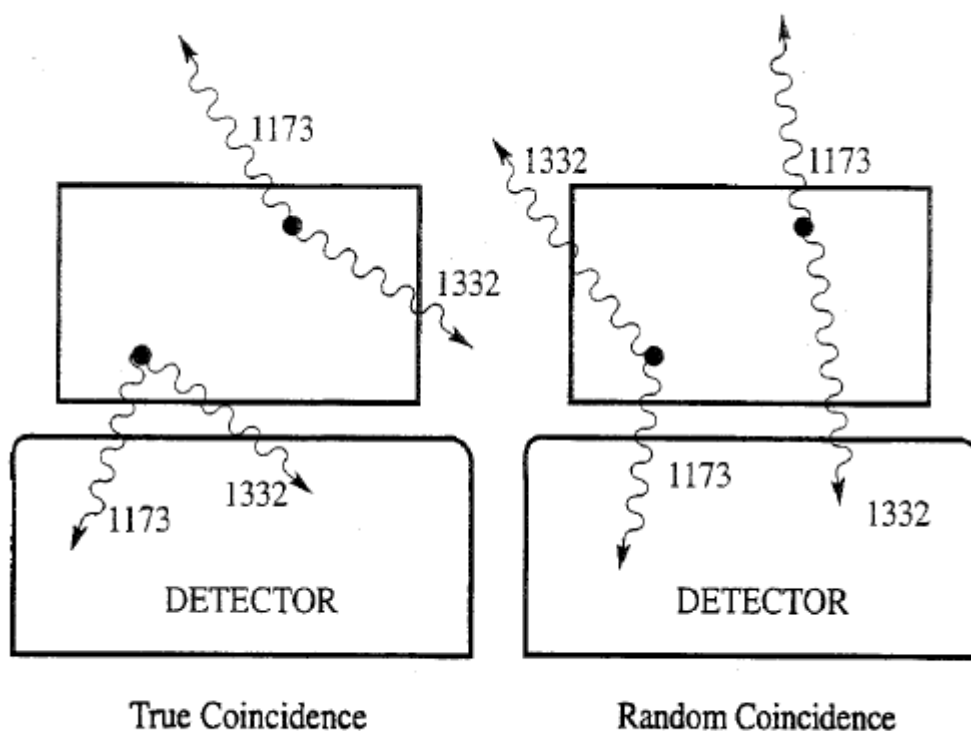


Figure 1. Examples of True Coincidence (Coincidence Summing) and Random Coincidence (Random Summing)

The two numbers shown in Figure 1 correspond to the two primary gamma photons produced during radioactive decay of Co-60. At FUSRAP sites such as the Maywood Superfund Site where the contamination levels, and therefore the count rates, are relatively low, the contribution from random summing is also low as illustrated in the example in TABLE I.

TABLE I. Random summing contribution to Maywood sample activity

Analyte	Yield ^a	Efficiency ^b	Sample Count Rate (cpm)	Sample Activity (pCi/g)	Random Summing Count Rate (cpm)	Random Summing Activity (pCi/g)	Contribution from Random Summing (%)
Ac-228	25.8%	0.01627	34.44	5.5172	0.028	0.00449	0.080
Pb-214	35.6%	0.03237	31.62	1.748	0.024	0.00133	0.076

- The yields correspond to the 911.2 keV line for Ac-228 and the 351.9 keV line for Pb-214.
- The efficiency values are taken from efficiency curves obtained from initial calibration of Canberra high purity germanium detectors.

One of the action levels at Maywood is that the sum of the activities of Th-232 (Ac-228) and Ra-226 (Pb-214) must be less than 5 pCi/g above background, so less than 6.64 pCi/g. Thus the activities shown in TABLE I illustrate the effect of random summing at or near the action level. At these activities, the relative contribution is very small compared to the counting uncertainty, which is approximately equal to the square root of the number of counts. For example, for the Ac-228 data in TABLE I, the count time is 60 minutes so the total counts are 34.44 X 60, or 2066 counts. The square root of 2066 is 45.5, so the approximate counting error is (45.5/2066) X 100, or 2.20%, which is about 27 times greater than the random summing error.

Library Energy and Yield

Gamma spectroscopy analysts will select an established library for the purpose of assigning “true” values to the energy and yield of a given radionuclide’s gamma photon. The yield of the gamma photon is the fraction of total gamma photons emitted during the decay process for a given radionuclide. Release of gamma photons is most commonly associated with beta decay, and typically several gamma photons, each with a different energy, may be emitted for a given beta decay event. To illustrate the potential inaccuracy of these assignments, one should look at the energy and yield values assigned to a given radionuclide by different libraries over time.

MARLAP recommends obtaining calibration data from the National Nuclear Data Center at Brookhaven National Laboratory (www.nndc.bnl.gov/nndc/nudat/)[4]. Another source is the Idaho National Laboratory Gamma Ray Spectrum Catalogue [5].

The following example, experienced at the Maywood onsite laboratory, illustrates a source of bias. The laboratory was originally using a yield of 29% for the 911.2 keV line of Ac-228. It began using the Brookhaven library which had a more up-to-date value for the yield of 25.8%. The yield dropped by 12.2% causing the Ac-228 activity values to increase by the same amount. The average Ac-228 obtained for the LCS had been biased low by about 14% and so now was more accurate. In addition, the yields for two of the Pb-214 lines changed as illustrated in TABLE II.

TABLE II. Relative yields for two Pb-214 energy lines in two different libraries

Old Library		Brookhaven Library	
<i>Pb-214 Energy</i>	<i>Yield</i>	<i>Pb-214 Energy</i>	<i>Yield</i>
351.99 keV	37.1%	351.93 keV	35.6%
295.22 keV	19.2%	295.22 keV	18.42%

On a relative basis, and assuming that the newer Brookhaven library is the more accurate value, the yields of both the 351.99 keV line and the 295.22 keV line went down by about 4.0% relative. This translates to an increase of 4.0% in the activity of Pb-214 since the fractional yield is in the denominator of the activity equation. So assuming the Brookhaven library is the more accurate library, the measured activities of Ac-228 and Pb-214 had low biases of 11.0% and 4.0%, respectively.

Instrument Calibration

CALIBRATION STANDARD DENSITY

The calibration standard used for testing project soils using gamma spectroscopy is provided in the geometry of choice (e.g., Marinelli beaker, tunacan, filter, etc.) and contains a soil such as a Griffin soil (high calcium quicklime) of uniform particle size range and density of 1.55 gcm^{-3} . Sample densities will vary from the calibration standard density so sample analyte signal efficiencies will be greater (if the sample soil density is $<1.55 \text{ gcm}^{-3}$) or less (if the sample soil density is $>1.55 \text{ gcm}^{-3}$) than that determined by the efficiency curve. Calibrations using mixed gamma sources can be adjusted to account for differences in density and composition between the calibration source and a given sample [6].

The calibration source certificate will typically provide the activity, activity uncertainty, analysis date and time, half-life, energy, and branching ratio of each radionuclide in the standard. The calibration standard supplier will provide an activity uncertainty which is the total propagated uncertainty (typically due mostly to the counting uncertainty) of the measured value. However, errors in the value of the half-life and branching ratio or yield, will contribute directly to measurement bias. This bias is transferred directly to the lab which purchases the standard and assumes that the activity is accurate.

There is an uncertainty associated with the activity assigned to each radionuclide in the calibration source and that uncertainty is typically found in the certificate that accompanies a given source. For the mixed gamma standard used to analyze soil samples at the Maywood project laboratory, the activities and uncertainties are shown in TABLE III.

TABLE III. Mixed gamma standard radionuclide uncertainties

Radionuclide^a	Activity, γps^b	U, relative expanded 2σ uncertainty, %
Am-241	1635	3.5
Cd-109	2334	4.7
Co-57	1265	4.1
Ce-139	1769	3.9
Hg-203	3592	3.8
Sn-113	2465	3.9
Cs-137	1636	4.0
Y-88 (898 keV)	6029	3.9
Co-60 (1173.2 keV)	3042	4.0
Co-60 (1332.5 keV)	3042	4.0
Y-88 (1836.1 keV)	6383	4.0

- a. Calibration source from Eckert & Ziegler Analytics; ref. NIST Technical Note 1297, "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results" [7].
- b. γ ps : gamma photons per second

Small differences between the calibration standard geometry and the sample geometry will cause an error. Differences in the source-to-detector positioning can also lead to errors.

Counting uncertainty of the calibration is reduced by accumulating as many points as practical. A good goal is a counting uncertainty of one percent or less for the standard deviation of the number of counts. For example, using the rough estimate that the standard deviation of the total counts is equal to the square root of the total counts, if one obtains 10,000 counts, then the relative error would be (Square root of 10000)/10000 = 100/10000, or 1%.

Interesting Bias Scenario

Additional error can enter into a system when considering the uncertainty in the activity of the radiological standard added to the LCS and MS samples. One notable error was encountered at the Maywood lab with a vendor- purchased LCS sample. The LCS contained three analytes of interest but we will focus on the Ac-228. Typically, one might expect an Ac-228 standard to contain the desired activity of its parent, Ra-228, which decays to Ac-228. The total Ra-228 activity of 3.5 pCi/g in this standard came from two sources: first, 1.19 pCi/g of long-lived Th-232 from background soil (which then decays to Ra-228) and second, 2.31 pCi/g of short-lived Ra-228 (5.75 year half-life) which is spiked into the background soil. This resulted in an LCS sample which was not decaying simply with the Ra-228 half life (and therefore couldn't be correctly decay corrected using the Ra-228 half life), but had continual ingrowth from the Th-232 parent, resulting in larger "effective" half life. The effective activity can then be expressed as follows:

$$A_t = 1.19 \text{ pCi/g} + A_0(e^{-\lambda t}) \quad (\text{Eq. 1})$$

Where 1.19 pCi/g = activity of the long-lived Ra-228 derived from Th-232 in background soil
 $A_0(e^{-\lambda t})$ = decay rate term to account for decay of the 2.3 pCi/g of Ra-228 spiked into the background soil
 $\lambda = 0.693/t_{1/2}$ = decay rate constant for Ra-228, where $t_{1/2}$ = the half-life for Ra-228 of 5.75 yrs.

So one source of bias is the decay of Ra-228, which at least initially was not decay-corrected. A second complicating factor, which was described in the Library Energy and Yield section above, is that the yield used for the Ac-228 911.2 keV line was biased high by 12.2%, which caused a low bias of 12.2% in the activity determination since the yield is used in the denominator. Between February 2011 and September 2012, the low bias increased (became more negative) due to the decay of the Ra-228 in the LCS as illustrated in TABLE IV.

TABLE IV. Decrease in the Maywood gamma spectroscopy LCS Ac-228 activity over time

Date	Activity after Decay Correction	Activity after Decay Correction + Reduction Due to High Yield of Ac-228 911.2 keV Line
11/22/2010	3.50	3.07
2/10/2011	3.44	3.02
5/10/2011	3.37	2.96
8/10/2011	3.31	2.91
11/10/2011	3.25	2.85

2/10/2012	3.18	2.80
5/10/2012	3.13	2.74
8/10/2012	3.07	2.69

The gamma spectroscopy library was changed on September 5, 2012, which eliminated the 12.2% bias, and the activity of the Ac-228 in the LCS was subsequently decay-corrected, which eliminated these two very significant sources of bias.

Efficiency and Energy Curve Uncertainties

The error in the slope of each curve will contribute to bias. The error which may arise from inaccurate assignment of a library energy or yield for a given radionuclide will contribute directly to bias as described above in the library energy and yield section. The components used for the uncertainty in the efficiency include the errors due to the uncertainties in the calibration source activities, and the uncertainty in the fit of the efficiency curve.

Alpha Spectrometry

In alpha spectroscopy, measurement bias from sample preparation may arise from sample losses (theoretically not an issue if a tracer is used), uneven distribution of precipitate on a planchet, pipette volume error, and sample volume error. Sample counting errors may be due to coelution of peaks (for example Th-229 and Th-230), calibration standard activity uncertainty, differences in efficiency between calibration standards and samples (sometimes caused by uneven distribution of precipitate on the sample planchet), detector fouling as a result of alpha recoil, and factors which cause poor peak shape.

Sample Preparation

Sample losses are a source of negative bias, although theoretically this is not an issue if a tracer is used. The tracer typically selected is one that is an isotope of the same element as the isotope of interest. In this case, the two isotopes will behave in the same manner during all sample preparation steps and so there will be no bias due to the sample preparation. Bias could still appear in the instrument measurement step. If the radioisotope of interest and the tracer isotope are different, but similar elements (such as Ba-133 used in the determination of Ra-226), some small bias may appear in the sample preparation step. Another source of bias during sample preparation is uneven distribution of precipitate on a planchet and the pipette volume errors for addition of standards to the Laboratory Control Sample and the addition of tracers to all samples.

Instrument Measurement

Differences in efficiency between that obtained during calibration with the zero-mass electroplated source, and the sample which has a small mass will lead to measurement bias. One would expect the efficiency of the electroplated source to be higher than that for the sample, thus leading to a low bias. For example, an electroplated source may yield a typical efficiency of 22%. For the Ra-226 method employed at the Maywood laboratory, the sample preparation yields a barium-radium sulfate coprecipitate that weighs approximately 3.5 mg. Even this small mass will reduce the efficiency from 22% to approximately 20.3% (reduction based upon observed alpha efficiencies at various masses on the gas proportional detector). Such a reduction creates a low bias in the calculated activity of approximately 7.7% $((22 - 20.3)/22) \times 100$. The alpha standard activity has a two sigma uncertainty of about 2.6%.

Overlapping peaks will create a positive or negative bias. A good example is Th-229 and Th-230. Th-229 is a tracer used in the testing of water samples for the presence of Th-228, Th-230, and Th-232. Even though thorium is not regulated in water, and is not expected to be present in water due to its extremely

low solubility, the Maywood project tests wastewater samples and environmental monitoring samples for the presence of thorium isotopes for information purposes. Th-230 is typically non-detect in these water samples. However, the overlap of the Th-229 peak with the Th-230 region of interest creates a low activity Th-230 peak that ranges in amplitude from about 0.2 pCi/L to 0.6 pCi/L. The Th-229 spike activity was reduced in an effort to reduce the peak overlap into the Th-230 region of interest. This caused a reduction of about 64% in the median Th-230 ghost peak activity (from 0.25 pCi/L to 0.09 pCi/L).

Detector fouling caused by alpha recoil will typically result in higher backgrounds over time. Detector backgrounds, which are measured monthly at the Maywood laboratory, provide a measure of potential detector contamination. Given the low activity and relatively small number of water samples measured by the alpha spectrometry detectors, increases in backgrounds caused by recoil have not been an issue.

Gas Proportional Detectors

For measurements using gas proportional detector counting systems there are multiple sources of potential error or bias.

Sample Preparation

Sample preparation may be one source of error that is often overlooked. This type of error may have several contributors including sample volume measurement error, pipette volume error, sample losses during evaporation or transfer, activity in the fine particulate fraction (samples for GA and GB are not filtered), negative bias due to incompleteness of precipitation of alpha emitters for Method 7110C sample preparation, and incompleteness of removal of beta emitters in Method 904.0 for Ra-228. The author has previously investigated the use of Total Propagated Uncertainty calculation to determine the contribution of these types of errors to overall sample error and determined while individual impacts may be small, compounding small errors in sample preparation and measurement can become appreciable when multiple steps are involved [12]. While the previous investigation showed that the sample volume error ranged from only 0.02% to 3.2% of the total propagated uncertainty of the systematic errors (errors from counting, efficiency and volume), random errors such as loss of sample during evaporation and sample transfer may be significant. Such larger errors will be evident when biases observed for LCS and performance evaluation samples are larger than what one would expect based upon systematic errors alone.

Instrument Measurement

Instrument counting errors may include improper selection of a curve fitting algorithm. Curve fitting should be discussed and reviewed with the Project Team, and the underlying errors present in the chosen curve should be evaluated to determine whether there is an appreciable contribution to laboratory uncertainty. A recent change in the curve fitting algorithm resulted in a change, depending upon the detector, of from 2% to 4% relative at zero mass. Such a change has a direct impact on the LCS measurement which has a zero, or near-zero mass. Differences between the salt composition used for the efficiency curve versus the salt compositions of samples may also play a factor in efficiency curve error contribution. An earlier study [13] showed that efficiency curves constructed from tap water were more representative of the types of water samples analyzed at Maywood than curves constructed using sodium chloride.

In addition to salt composition, differences in efficiency due to the difference between the energy of the alpha or beta emitter used to construct the curve versus the energies of the alpha or beta emitters in the sample need to be considered. For example, the lone alpha emitter used to construct the alpha efficiency curves is Th-230, while the primary contributors to alpha activity in water at the Maywood site are likely to be U-238, U-234, Ra-226, and possibly polonium isotopes. For gross beta measurement, Sr/Y-90 is

used to construct the efficiency curves while the primary contributor to gross beta activity at Maywood is likely to be Ra-228 and Ac-228, and also isotopes of lead, bismuth and thallium.

Other typical errors which should not be overlooked include alpha to beta crosstalk, and the contribution of natural potassium-40 to the gross beta measurement.

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