High Resolution Gamma-Ray Spectrometry Analyses for Normal Operations and Radiological Incident Response

US EPA NAREL, Dr. John Griggs
and
Environmental Management Support (EMS)

During the past 8 years, EPA has sponsored radiochemistry training for state laboratories and a series of proficiency test samples containing activation and fission products to state, commercial and government laboratories. The objective of these programs was to provide laboratory staff with the basics of radiochemistry, and in particular gamma spectrometry. One of the realizations coming from the training and PT sample evaluations was that many technical staff had only a brief introduction to several areas of radiochemistry. In particular, gamma spectrometry was seen to be a weak area. The technical information regarding the practice of gamma ray spectrometry was not well consolidated into one document, and the technical aspects of dealing with high activity samples versus environmental samples was not addressed in significant depth anywhere. Also needed was guidance on how to use different software functions based on the type of samples being analyzed.

The guide, “High Resolution Gamma-Ray Spectrometry Analyses for Normal Operations and Radiological Incident Response” was written to provide new and experienced users with a new reference on the topic that addressed some of the newest features of how the gamma spectrometry system functions and how to review the data. This workshop will engage the audience in the materials presented in the guide and demonstrate the utility of the document.

Workshop Goal:
Present information contained in the recent EPA document with the above title.
Reinforce basic gamma ray interactions and analysis using high resolution gamma ray spectrometry.

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High Resolution Gamma-Ray Spectrometry Analyses For Normal Operations and Radiological Incident Response

Sponsored by
Dr. John Griggs, National Analytical and Radiation Laboratory (NAREL)

Purpose for Workshop

- The guide will be issued in the near future. We want to:
  - Overview the contents of this new guide
  - Have practitioners recognize that this is a basic reference
  - Contents apply to all types of gamma spectrometric analysis

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A Collaborative Effort

EMS Contractors Contributing to this document

- David McCurdy,
- Robert Shannon,
- Stan Morton,
- Daniel Montgomery, and
- Sherrod Maxwell

Independent Industry Reviewers

- Doug Van Cleef
- Steve Sandike

Is there a Need?

The incentive to develop this guide came from two significant observations:

- Most laboratory staffs have not had significant experience dealing with high activity concentrations in samples from a nuclear or radiological event
- An observation that many practitioners principally rely upon the software analysis of the gamma spectrum (even though some reported results are improbable).

Introductory Topics in the Guide

- Modes of radioactive decay
- Review of the interactions of gamma rays with matter (in particular with the detector)
- Identification of anomalous photopeaks
- ***Radioactive decay and parent-progeny relationships***
- Potential threat radionuclides from an IND, RDD or another radiological event

Gamma Spectrometry Specific Topics

- Software Preset Functions
- Selecting Detectors
- Sample Preparation and Selection of a Detection Criterion
- Detector Calibration
- Data Verification and Validation

Interactive Discussion

- We encourage interactive discussion during the presentation
- No Hiding!

Source Term Radionuclides

What you need to measure should influence how you approach your measurement…

Bob Shannon

Threat or Accident Radionuclides

- Source terms vary by event
  - RDD *(radiological dispersal device)*
    - Longer-lived radionuclide(s), e.g., ^{241}Am ^{241}Co
    - Pure alpha or beta emitters, e.g., ^{210}Po, ^{90}Sr/^{90}Y `
  - IND *(improvised nuclear device)*
    - Complex mixtures of shorter- and longer-lived fission products
  - Nuclear power plant related incident
    - Complex mixtures of shorter- and longer-lived fission products
    - Will generally contain more activation products than an IND (incident dependent)

Threat or Accident Radionuclides (cont.)

- Commercial/industrial incident
  - Radioisotope thermoelectric generators (RTG)
    - ^{90}Sr, ^{238}Pu, ^{237}Np
  - Medical isotopes
    - ^{131}I, ^{103}Pd, ^{192}Ir
  - Well-logging devices
    - ^{60}Co, ^{124}Sb, ^{140}La
  - Radiography
    - ^{60}Co, ^{137}Cs, ^{75}Se, ^{241}Am
- And others…

Alpha Emitters

Radionuclide	Gamma Energy keV	Gamma-ray Abundance	Half-Life	Radionuclide	Gamma Energy keV	Gamma-ray Abundance	Half-Life
Am-241	59.5	35.9%	432.7y	Ra-226	186.2	3.64%	1.599×10^3y
Cm-242	44.1	0.0035%	162.8d	Th-228	84.4	1.22%	1.91y
Cm-243	277.6 228.2	14.0% 10.6%	29.1y	Th-230	67.7	0.38%	7.56×10^4y
Cm-244	42.8	0.26%	18.1y	Th-232	63.8	0.0263%	1.4×10^{10}y
Np-237	86.5	12.4%	2.14×10^6y	U-234	53.2	0.0123%	2.46×10^5y
Pu-238	43.5	3.92%	87.7y	U-235	185.7	57.0%	7.04×10^8y
Pu-239	51.6	0.0272%	2.41×10^4y	U-238	49.6	0.064%	4.47×10^9y
Pu-240	45.2	0.0447%	6.56×10^3y	U-Nat	185.7 (^{235}U)	57.0%	4.47×10^9y

Alpha emitters with low abundance gamma rays are not suitable be used for low-level determinations. They are effective for identifying specific radionuclides when they may be present in high activities.

Beta Emitters

Radionuclide	Gamma Energy, keV	Gamma-ray Abundance	Half-Life	Radionuclide	Gamma Energy, keV	Gamma-ray Abundance	Half-Life
Ac-227 [1] Th-227	-- 236	-- 12.9%	21.7 y 18.7 d	Ba-140 La-140	537 1596	24.39% 95.4%	12.8 d 1.68 d
Bi-212	727	6.68%	60.6 min [2]	Mo-99 Tc-99m	740 141	12.26% 89%	2.75 d 6.01 h
Bi-214	609	45.5%	19.9 min [2]	Pd-103	39.7	0.683%	17.0 d
Co-57	122 136	85.6% 10.68%	271.8 d	Pb-210	46.5	4.25%	22.3 y [2]
Co-60	1173 1332	99.85% 99.98%	5.271 y	Pb-212	239	43.6%	10.6 h [2]
Cs-137 [1] Ba-137m	662	89.9%	30.0 y 2.55 min	Pb-214	352	35.6%	27 min [2]
I-125	35.5	6.68%	59.4 d	Pu-241[1] Am-241[3]	-- 59.4	-- 35.9%	14.3 y 432.6 y
I-129	39.6	7.51%	$1.57x10^7$ y	Ra-228 [1] Ac-228	-- 911, 338	-- 25.8%, 11.3%	5.76 y 6.15 h [2]
I-131	364	8.15%	8.01 d	Ru-106 [1] Rh-106	--- 511.9, 622	-- 20.4%, 9.93%	1.02 y 299 s
Ir-192	317	82.86%	73.8 d	Se-75	265 136	58.9% 58.5%	119.8 d

[1] Parent has no or low-abundance gamma ray. Progeny gamma ray(s) frequently used for inferential quantification.

[2] Decay progeny of ^{226}Ra or ^{224}Ra. Exercise care to ensure defensible assumptions are used when assigning half-lives in libraries.

[3] Am-241 is the decay progeny of ^{241}Pu. The extent of equilibrium in environmental samples is not generally known.

Beta Emitters (Fission Event)

Alpha Emitters	**Beta/Gamma Emitters**		
Am-241	Ba-140 / La-140	Mo-99 / Tc-99m[3]	Ru-103 / Rh-103
U-235	Ce-141	Nd-147 / Pm-147[2]	Ru-106 / Rh-106[3]
U-238[1]	Ce-143 / Pr-143[2]	Eu-155	Sb-125
Pu-238[1]	Ce-144 / Pr-144	I-131/Xe-131	Te-132/I-132[3]
Pu-239[1]	Cs-134	I-133	Zr-95 / Nb-95
Pu-240[1]	Cs-137[3]	Np-239	Zr-97 / Nb-97
Pu-241	Eu-154	Pm-151 / Sm-151[2]	
Activation Products			
Co-58	Ag-110m	Cr-51	Mn-54
Np-239	Co-60	Fe-59	Na-24

Notes:

[1] *Complex, high-activity mixture containing alpha emitter with low abundance gamma rays.*
[2] *"No Equilibrium" radionuclide pair*
[3] *Parent is low abundance or non-gamma emitter; May be possible to use progeny for quantification.*

Make Informed Assumptions About Samples

- A number of factors impact the fate and transport of radionuclides prior to sampling
  - Physical and chemical effects lead to fractionation
    - Volatility, solubility
    - Weathering, reactive particles, colloids
  - Analyte bound in insoluble/refractory materials (e.g., discrete radioactive particles, DRPs)
    - May not be subject to differential solubility and thus freeze ratios at time prior to sample collection
    - DRPs will likely complicate analysis (homogeneity)

Libraries - One Size Does Not Fit All!!

- Assumptions impact how results are interpreted
- Identify assumptions and limitations
  - Possible interferences (physical, chemical, spectral)
  - Inferential determinations
  - Issues with radioactive equilibria decay correction
- Document and disclose all assumptions and their impact on results

Match the Library to the Sample Type

- Match libraries to the source term and sample type
- Keep libraries as short and simple as possible
  - Primary and confirming line(s) for radionuclides of concern and lines as needed to resolve interferences
- Use suspect library to keep analysis library small
  - Better unidentified peak ID and shorter quant reports
  - Don’t use master library - build a suspect library with:
    - With all lines for radionuclides of concern for sample type
    - Lines for non-analyte radionuclides in the sample type
    - Lines for spectral features (e.g. x-rays, sum and escape peaks)
    - Can edit on-the-fly without risk of compromising results!

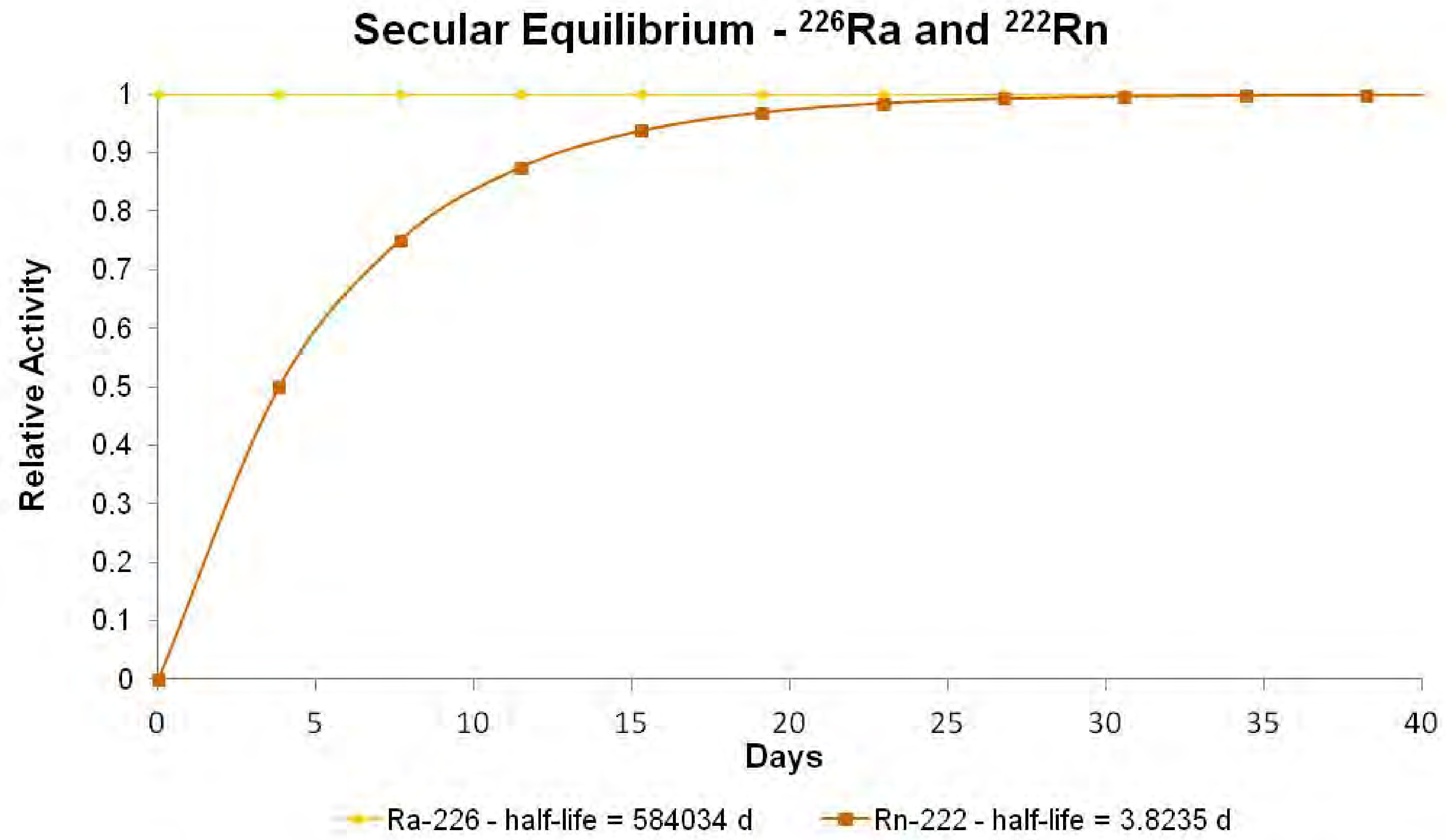
Radioactive Equilibria

What you need to know if you
want to decay correct…

Radioactive Equilibria

- Most of the gamma ray emitters in the previous tables are part of an equilibrium
  - For true equilibrium, the activity curves for parent and progeny will, at some point, be parallel.
- Three types of radioactive equilibria
  - Secular Equilibrium
  - Transient Equilibrium
  - No Equilibrium
- The equilibria are determined by the relative half-lives of the parent and progeny pairs

Secular Equilibrium



Equilibrium Ratio of Progeny-Parent

$$A_d^1 = A_d^0 e^{-\lambda_d \Delta t} + A_p^0 \left(\frac{\lambda_d}{\lambda_d - \lambda_p}\right)\left(e^{-\lambda_p \Delta t} - e^{-\lambda_d \Delta t}\right)$$

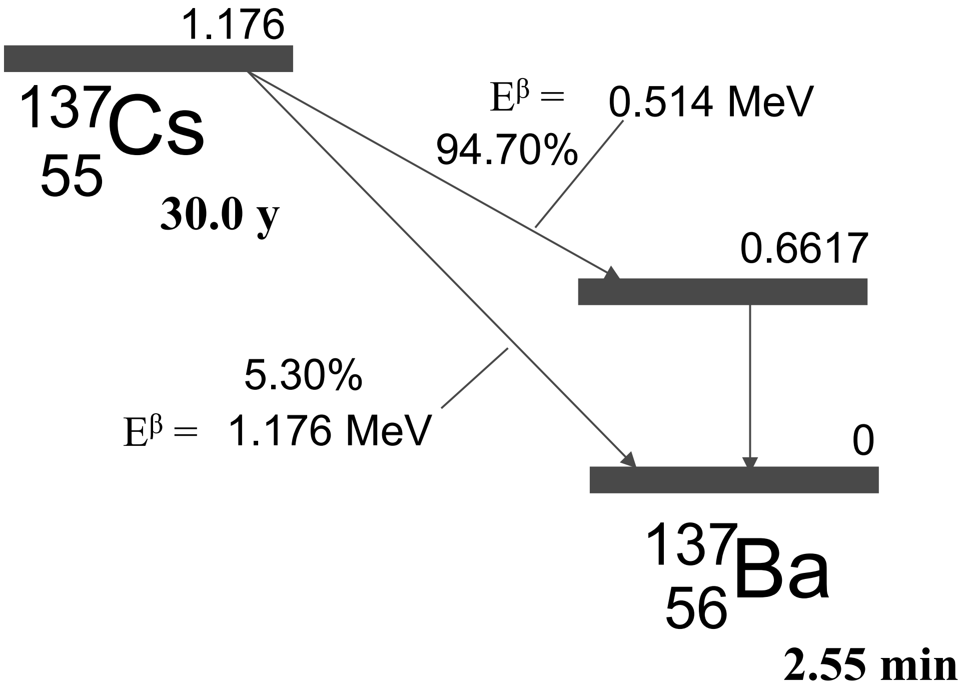
Bateman Equation
(first progeny)

$$\frac{A_d}{A_p} = \frac{\lambda_d}{\lambda_d - \lambda_p}$$

Ratio of progeny activity to parent activity at equilibrium

- Equilibrium is said to be achieved when the observed ratio of progeny-to-parent activity approaches the theoretical A_d/A_p
  - When progeny half-life << parent, the ratio of progeny to parent activity at equilibrium approaches 1 (secular equilibrium)
  - As progeny half-life approaches half-life of the parent, the ratio will be greater than 1 (transient equilibrium)
- After equilibrium, perform decay corrections using parent half-life and conventional gamma spec software (more later)

Decay Scheme for ^{137}Cs – ^{137m}Ba



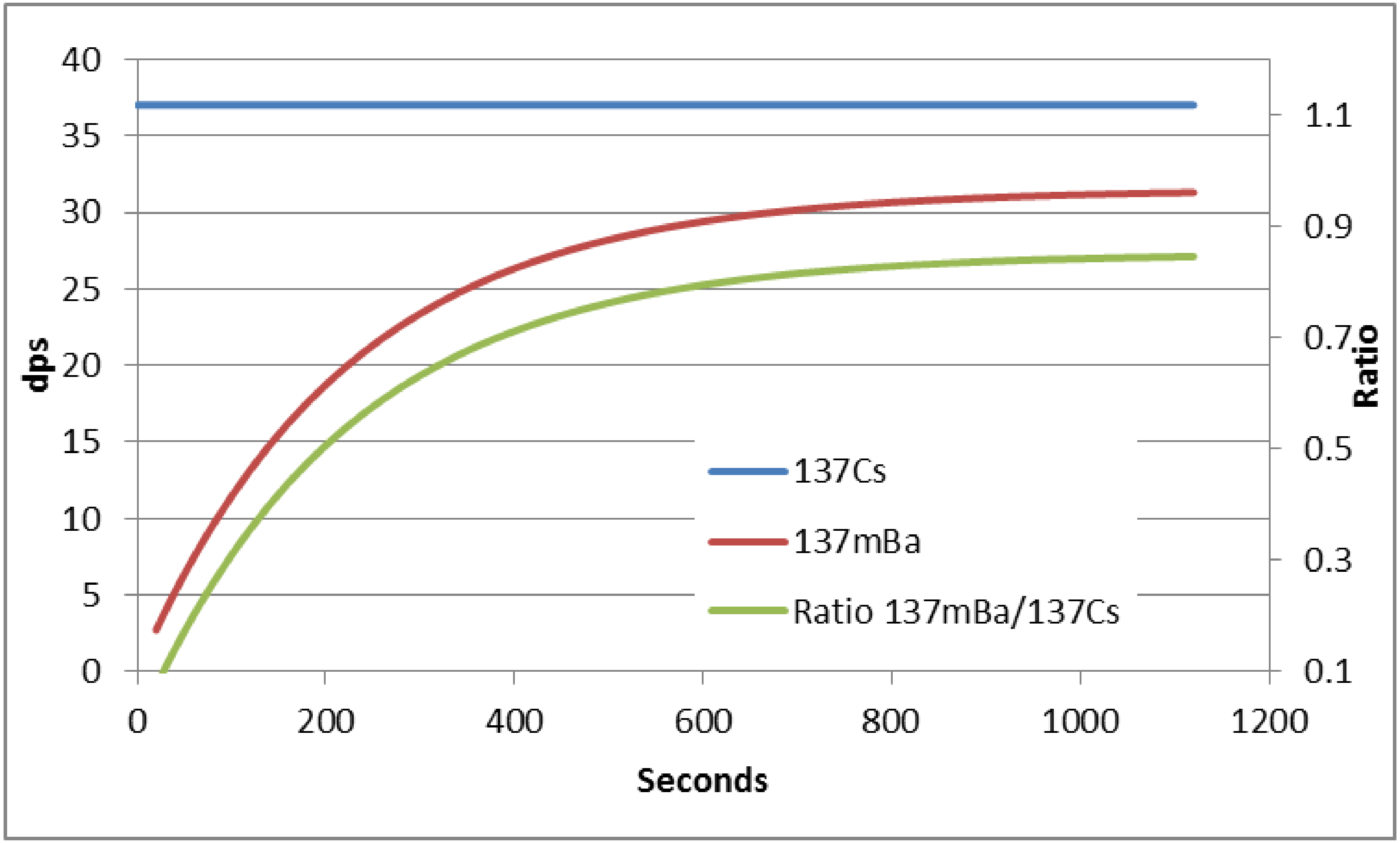
Internal conversion competes with isomeric transmission

	Energy (keV)	Intensity (%)
CE K	624.2	7.79%
CE L	655.7	1.40%
CE M	660.4	0.300%
CE N	661.4	0.0646%
CE O	661.6	0.00965%
	Total	**9.57%**

Gamma emissions relative to ^{137}Cs decay

^{137}Cs activity has an abundance value of 85.1 γ/100 decays (94.70% - 9.57%)

Decay Scheme Affects Equilibrium Ratios



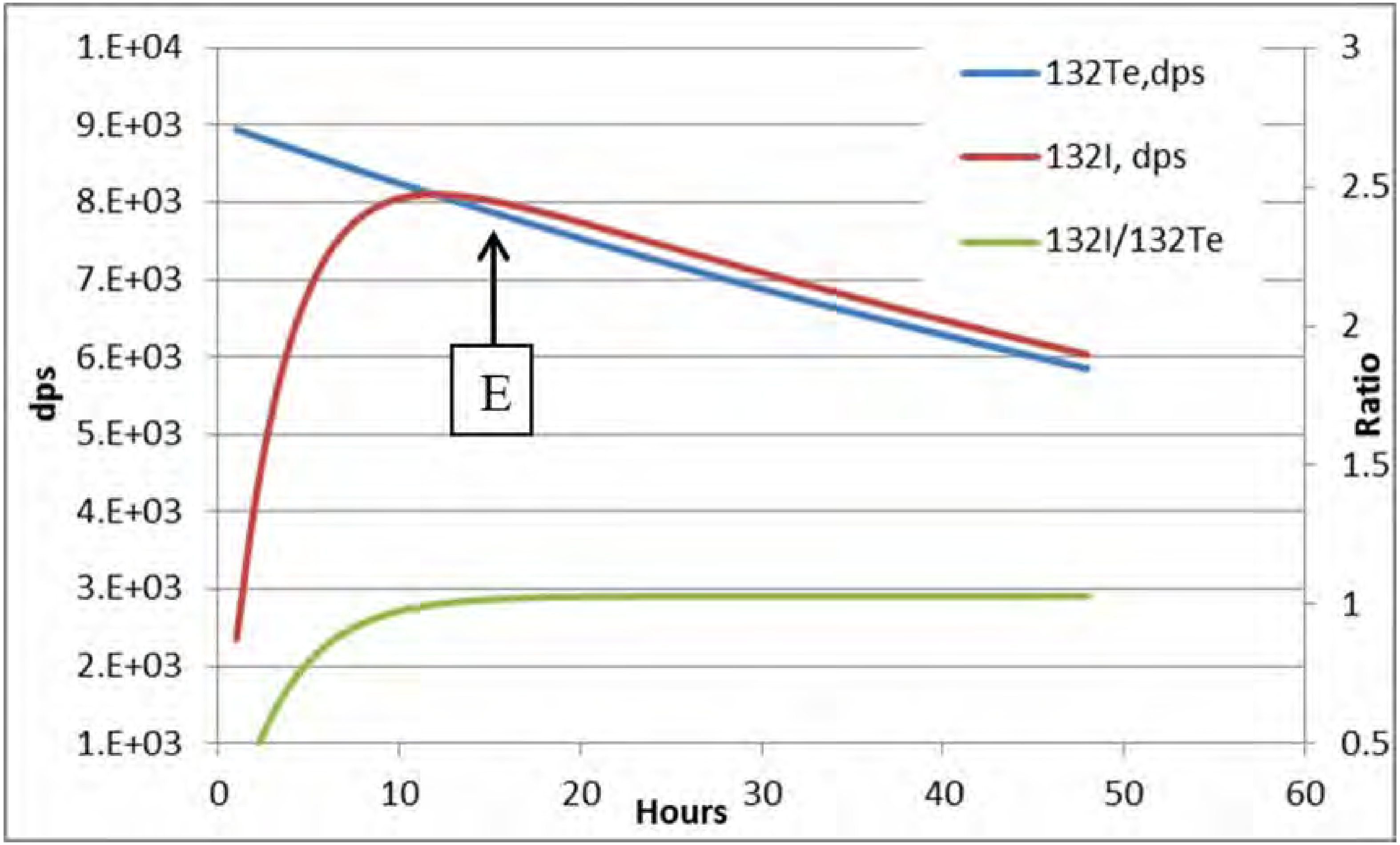
The ^{137m}Ba activity takes into account the branching from ^{137}Cs to ^{137m}Ba, and the internal conversion for the 662 keV gamma ray of ^{137m}Ba

How Long to Equilibrium?

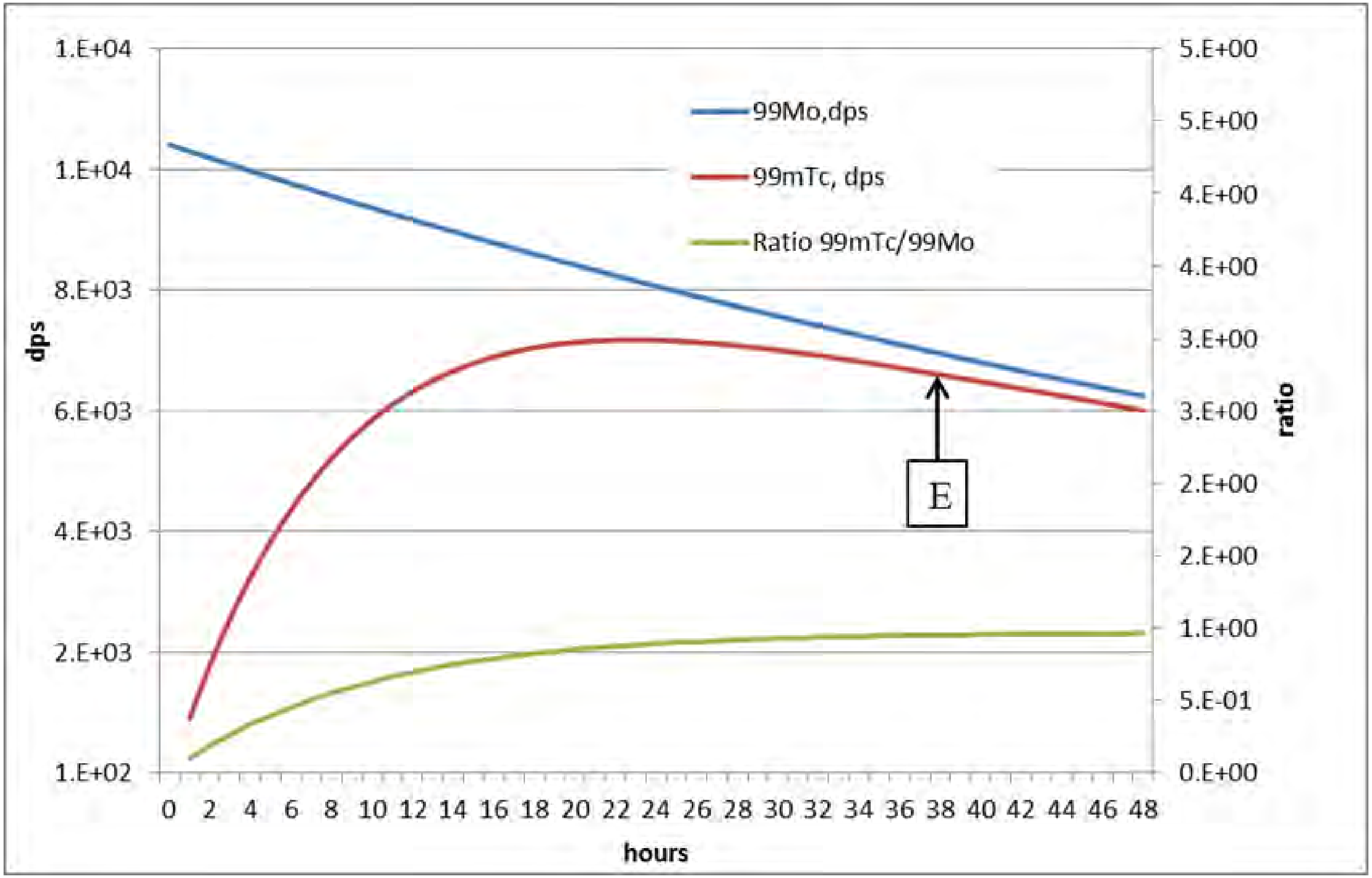
$$T_{\max activity} = \frac{(ln\lambda_p - ln\lambda_d)}{(\lambda_p - \lambda_d)}$$

- The time needed to maximum activity of the progeny depends on the half-lives of parent and progeny
  - Secular equilibrium occurs prior to $T_{\text{max activity}}$
  - Transient Equilibrium occurs after $T_{\text{max activity}}$
- Equilibrium is never really “achieved”
  - Activity curves *approach* parallel at equilibrium
    - Definition driven by needs (e.g., 95% or 99% of theoretical ratio of progeny to parent)
- Concepts don’t apply to “no equilibrium” case

Transient Equilibrium (I)

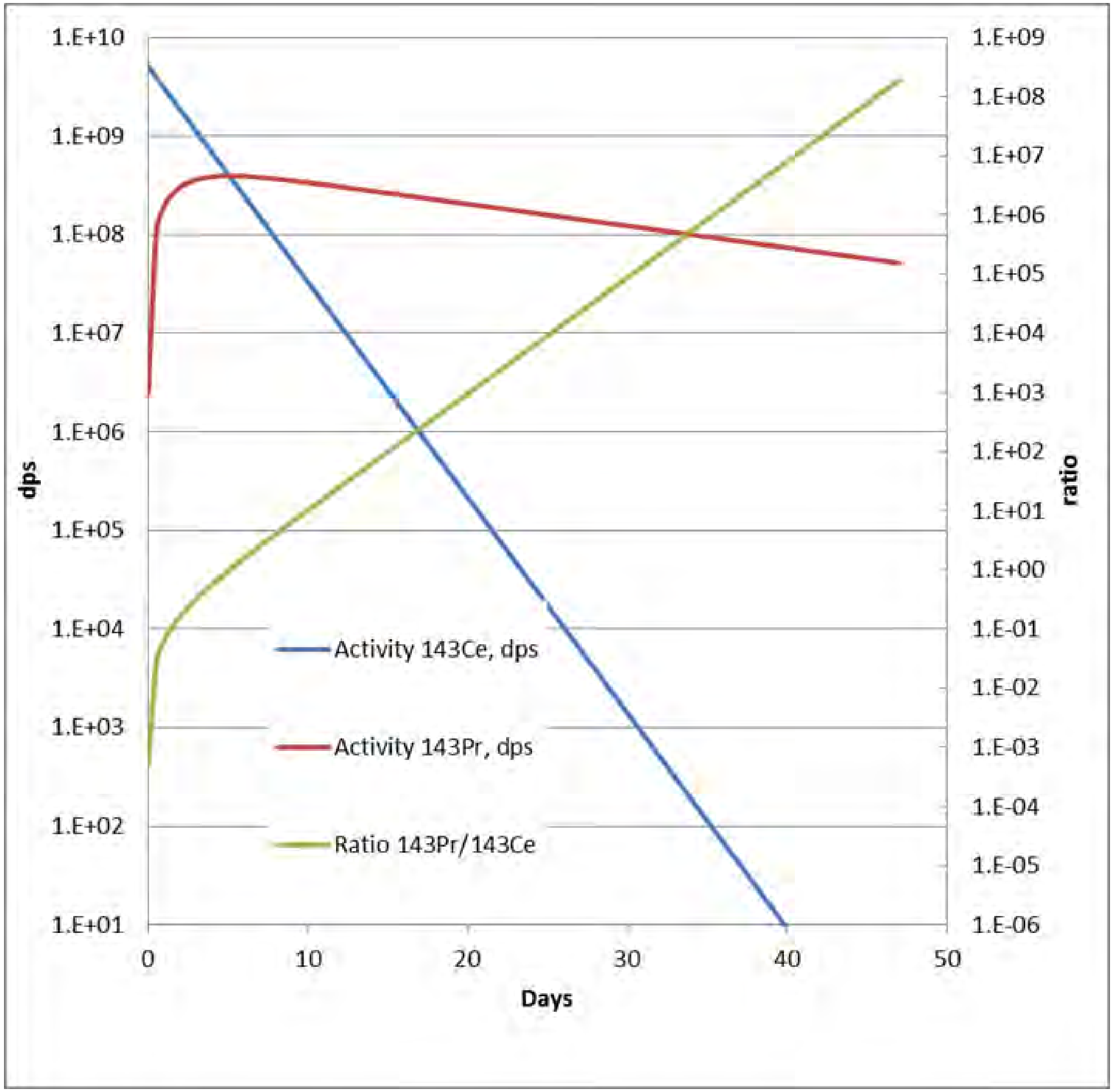


Transient Equilibrium (II)



Note: The ^{99m}Tc activity takes into account the branching from ^{99}Mo to ^{99m}Tc.

No Equilibrium



Equilibrium Pairs and Time to Equilibrium for Fission Event

Radionuclide Pair	**λ Parent (Days^{-1})**	**λ Progeny (Days^{-1})**	**Days to Peak Progeny Activity**	**Type of Equilibrium**	**Activity Ratio Progeny/Parent (Equilibrium)**
Fission Products					
^{95}Zr/^{95}Nb	1.08×10^{-2}	0.0198	67.3	Transient	2.20
^{99}Mo/^{99m}Tc	0.252	2.77	0.952	Transient	0.96
^{140}Ba/^{140}La	5.44×10^{-2}	0.413	5.65	Transient	1.15
^{106}Ru/^{106}Rh	$1.87x10^{-3}$	$2.0x10^{+3}$	6.94×10^{-3}	Secular	1.00
^{132}Te/^{132}I	0.217	7.3	0.496	Transient	1.03
^{131}I/^{131m}Xe	8.64×10^{-2}	0.0582	14.0	No Eq.	N/A
^{137}Cs/^{137}Ba	$6.31x10^{-5}$	391	0.0400	Secular	1.00
^{147}Nd/^{147}Pm	6.31×10^{-2}	7.23×10^{-4}	71.6	No Eq.	N/A
^{143}Ce/^{143}Pr	0.503	5.11×10^{-2}	5.06	No Eq.	N/A
Naturally-occurring Radionuclides					
^{238}U/^{234}Th	$4.25x10^{-13}$	0.0288	866	Secular	1.00
^{228}Ra/^{228}Ac	$3.29x10^{-4}$	2.58	3.48	Secular	1.00
^{228}Ra/(^{228}Ac)/^{228}Th	$3.29x10^{-4}$	$9.92x10^{-4}$	1660	Transient	1.50
^{226}Ra/^{222}Rn	$1.19x10^{-6}$	0.181	65.9	Secular	1.00
^{214}Pb/^{214}Bi	37	50.1	2.31×10^{-2}	Transient	3.82
^{212}Pb/^{212}Bi	15.6	16.6	0.157	Transient	1.10
^{210}Pb/^{210}Bi	$8.51x10^{-5}$	0.138	53.6	Secular	1.00

Sample Collection Can Impact Equilibria

- Sample collection issues may impact results
  - Is the sample homogenous?
  - Does the sample have multiple phases?
    - Gas-particulate
      - ^{131}I or noble gasses?
    - Aqueous with particulate/sediment
      - Filter or suspend?
      - Preserve?
    - Non-miscible liquids
      - Separate phases

Preservation Can Impact Equilibria - Liquids

- Optimally preserve samples in the field
  - Acidification for most radionuclides (e.g., metals)
    - pH 2 may not be sufficient for some radionuclides
    - Acidification can lead to loss of analyte (e.g., I_2)
  - Acidification will not stabilize all analytes
    - e.g., Zr - Fluorides will form soluble complex with Zr but it will precipitate some actinides and lanthanides
    - Many iodides, fluorides, sulfates, etc. may be insoluble
- There may be no single good preservation method - more than one sample may be needed

Preservation – Gases / Volatiles

- Noble gas may emanate from solid or liquid matrix *in any type of container*
  - ^{222}Rn, Xe, and Kr
- Noble gas may escape through container walls
- Consider thermal preservation for I_2 cartridges
- Distribution of gas may not match calibration
  - Rn and decay products may concentrate in headspace or on container surfaces
  - Filling void spaces in soil samples with mineral oil has been used ensure homogenous distribution

Gamma Ray Interactions with Matter

Bob Litman

Photoelectric Effect

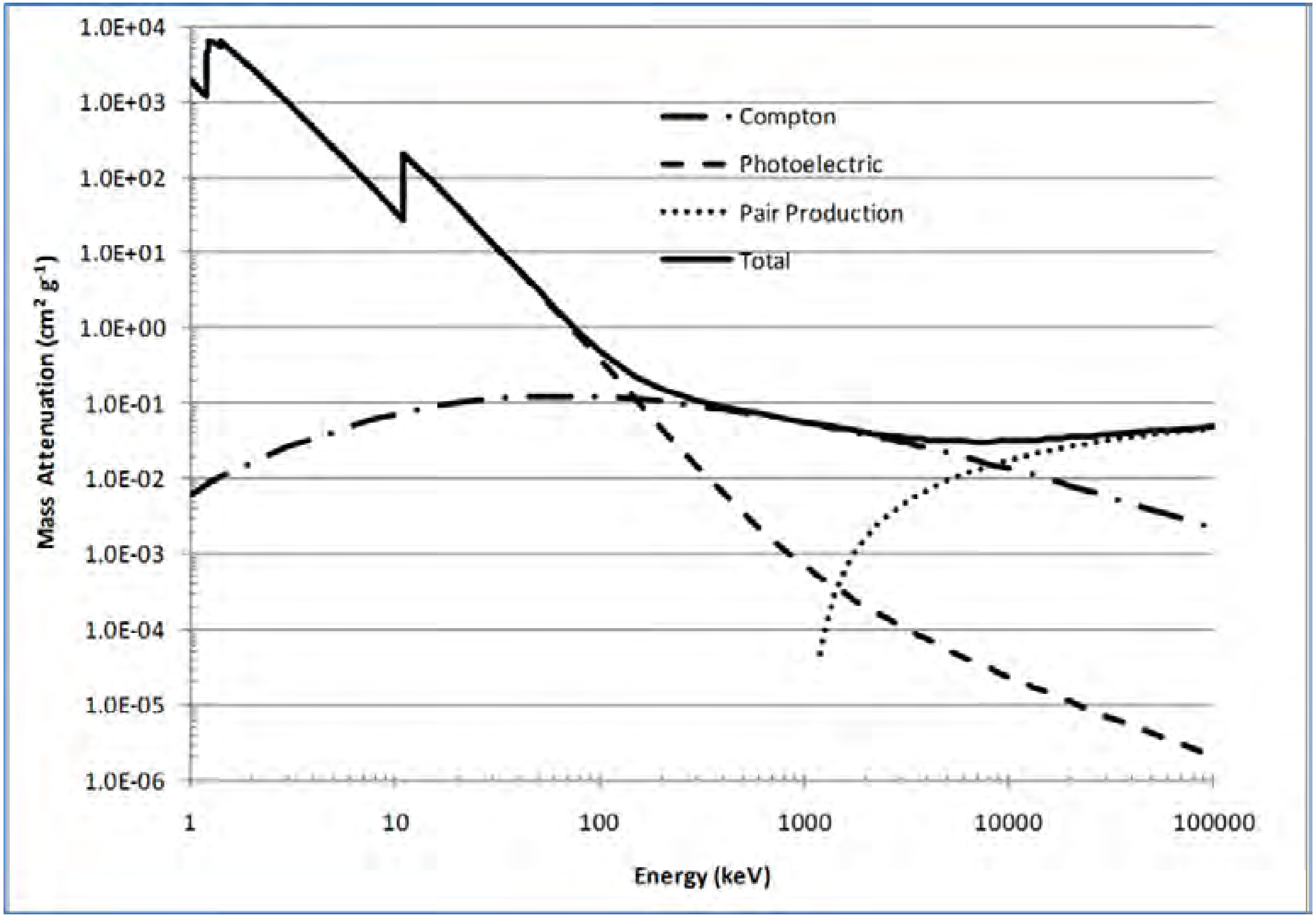
- A gamma ray interacts with a bound, detector electron,
  - Transfers all its energy to electron
  - Electron has sufficient energy to be promoted to the conduction band of the HPGe detector
  - Gamma ray no longer exists
- This is the interaction that yields the full energy peak (<u>FEP</u>) in the gamma ray spectrum

Affected by What?

The efficiency of detection of the FEP by the detector is affected by

- Detector size/shape
- Sample size/shape
- Average Z value of the sample matrix
- Average Z value of the sample container
- Material of detector ‘cover’

Probability of Interaction



Location of the “Edge”

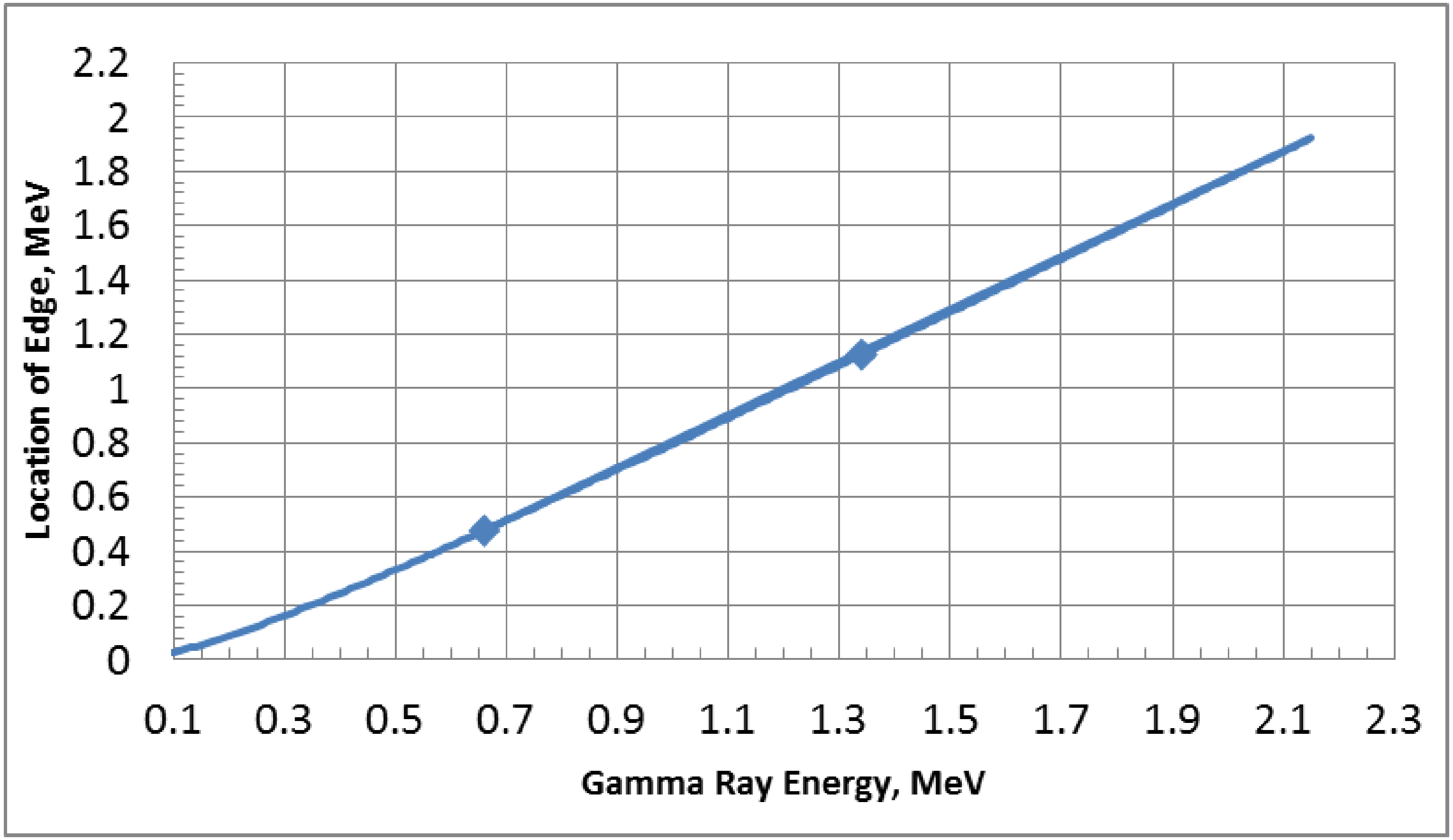
The energy relationship between where the edge occurs and the gamma ray that creates that edge can be calculated using the following formulas:

$$E_{\gamma}^{\min} = \frac{0.511 \times E_{\gamma}}{(2 \times E_{\gamma} + 0.511)}$$

The next equation identifies the location of the Compton edge,

$$E_{e^-}^{\max} = E_{\gamma} - E_{\gamma}^{\min}$$

Compton Edge Location



Importance of the Compton Edge?

- All gamma rays have a Compton edge and distribution
- Creates a change in the background:
  - Can hide low intensity gamma rays
  - Can increase and broaden background at low energy obscuring gamma rays below ~250 keV
- Can cause broadening of gamma rays that reside close to the "edge"

Compton Scattering: The Backscatter Peak

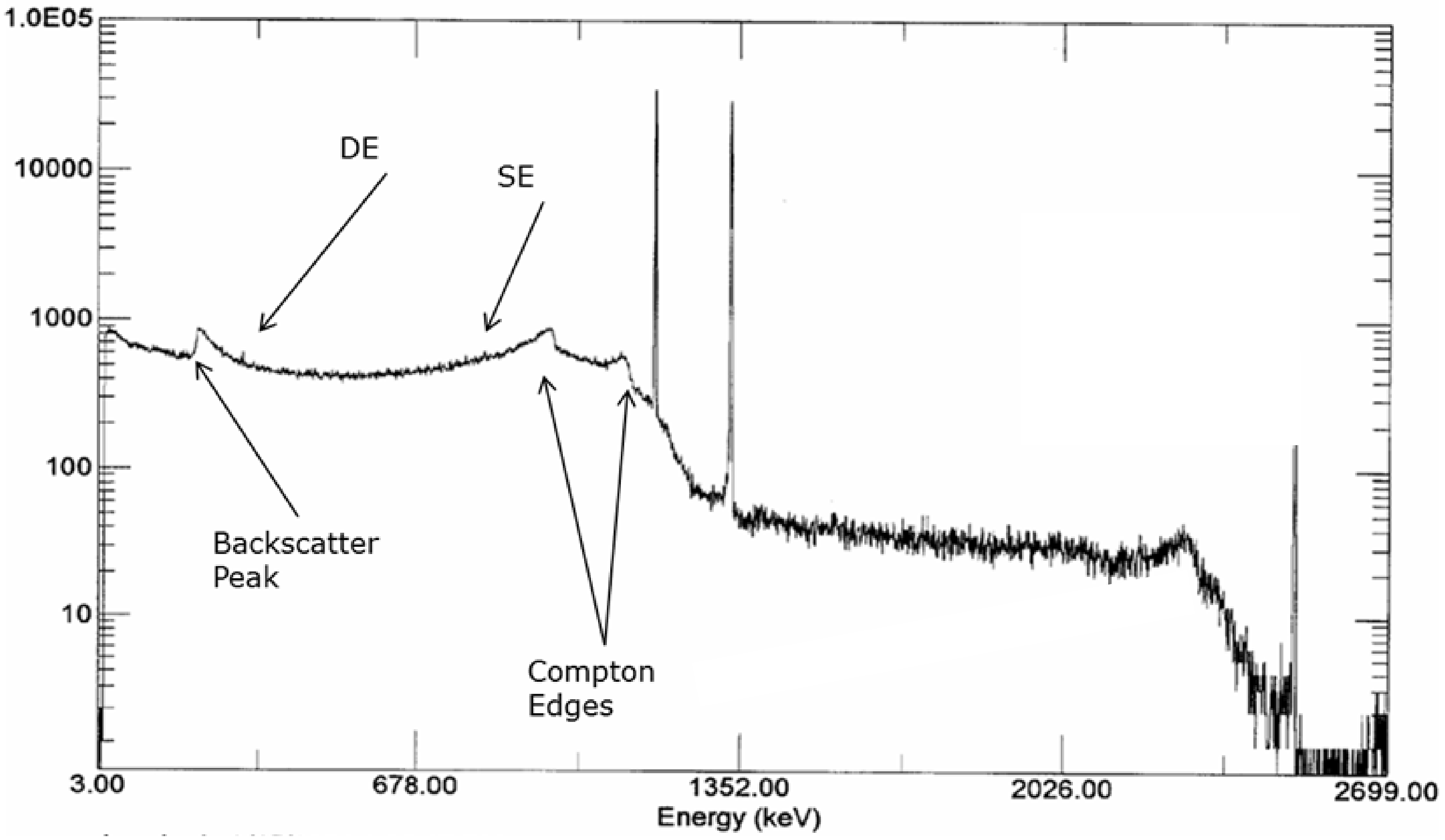
The minimum energy for a Compton scattered gamma ray is given by:

$$E_g^{\min} = \frac{0.511´\ E_g}{(2´\ E_g + 0.511)}$$

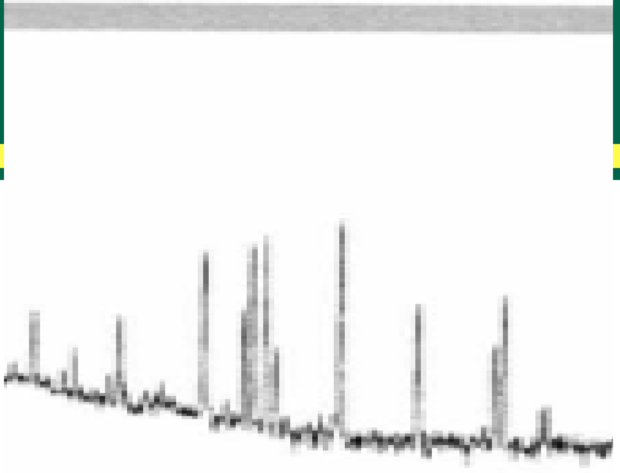
As the energy of the gamma ray $E_\gamma^{\min}$ increases, approaches 0.256 MeV.

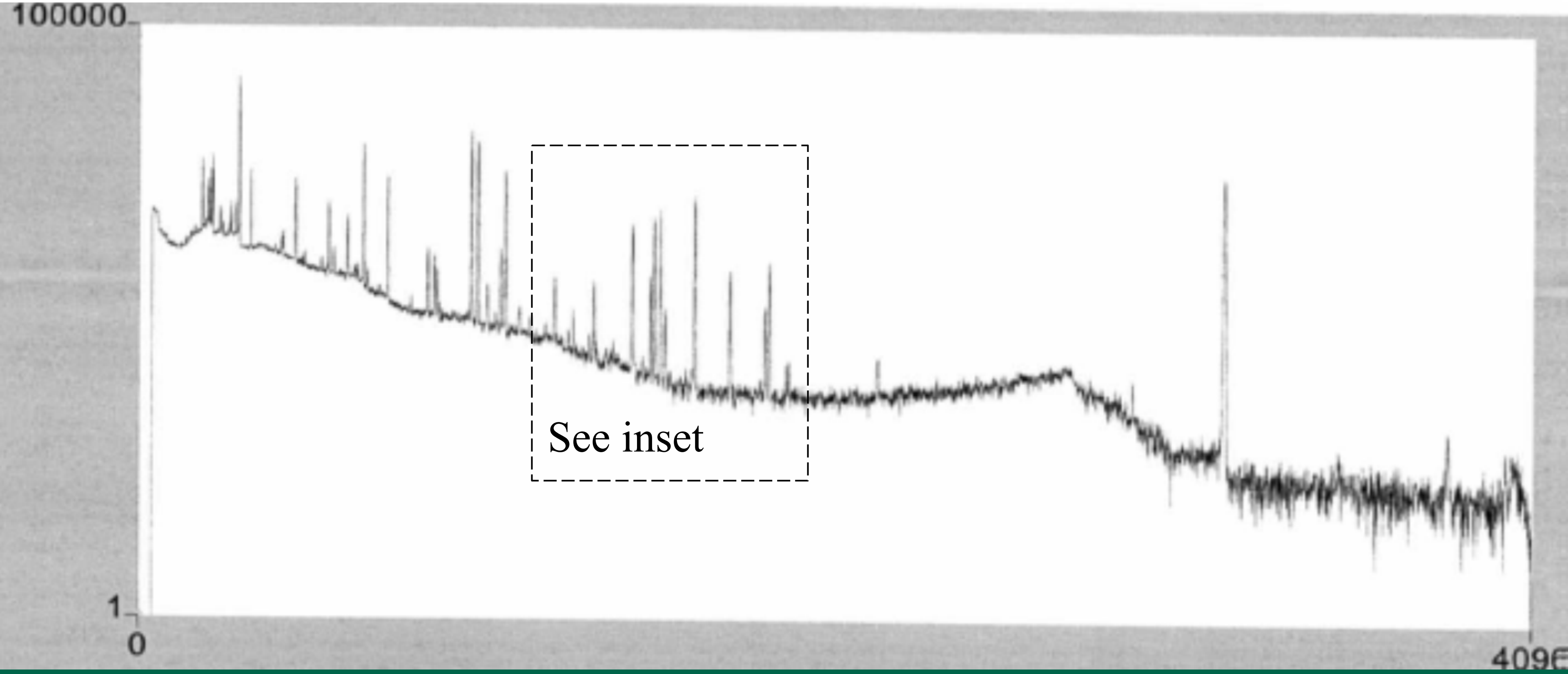
This appears as a broad peak below 250 keV

Co-60 Spectrum Showing Compton Edges

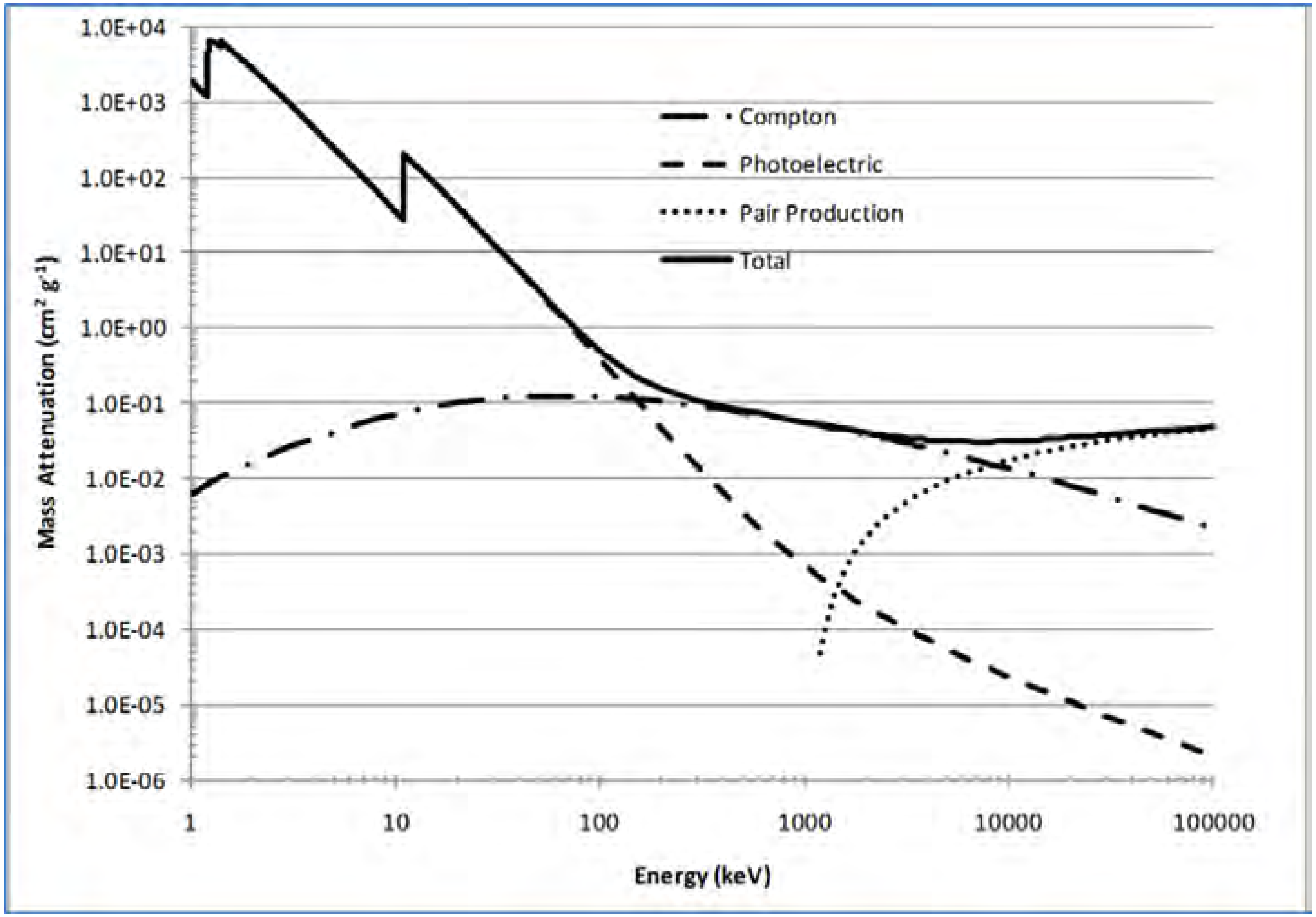


Effects of Compton Pile-Up





Probability of Interaction



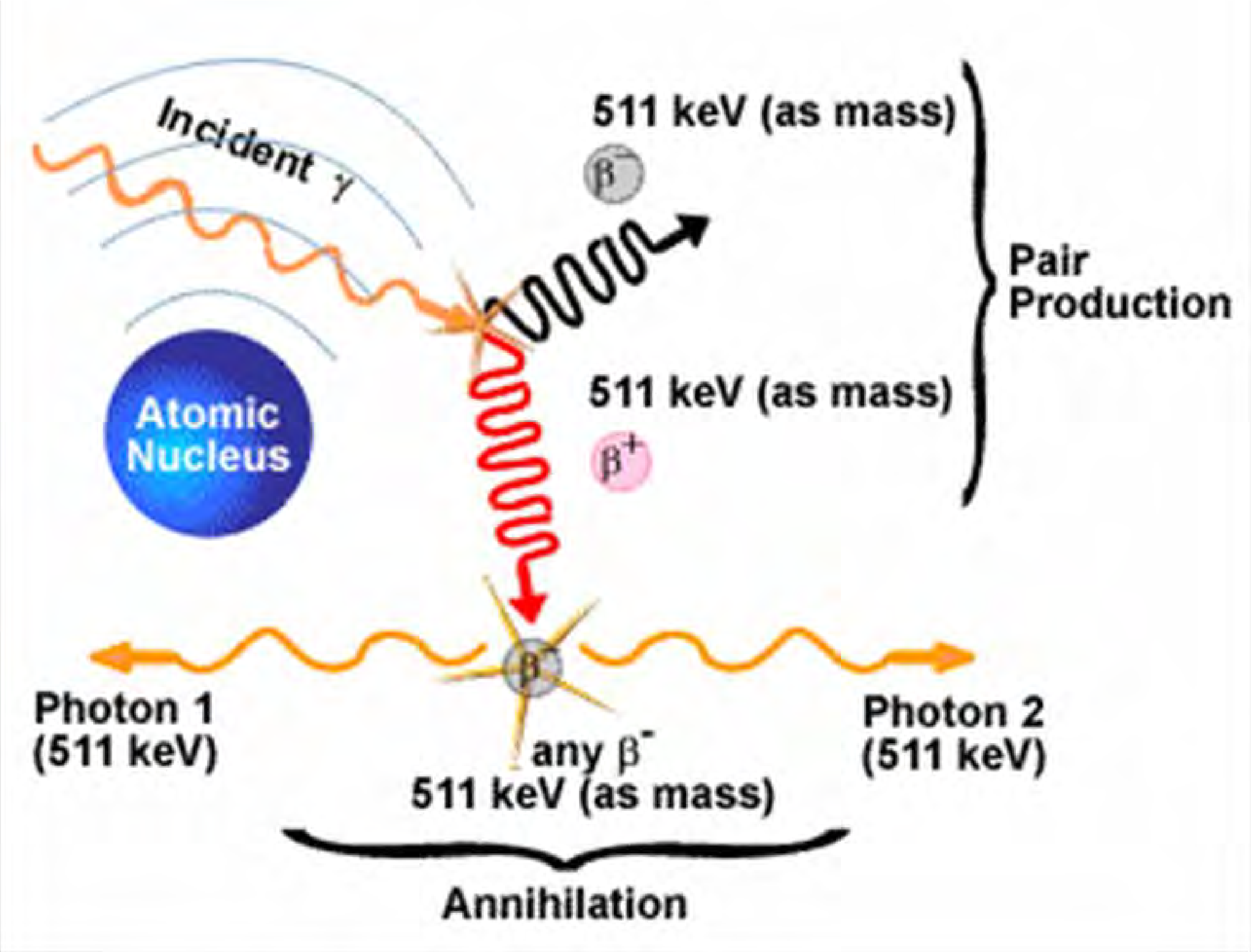
Pair Production (PP)

- Energy and matter are related based on the Einstein formulation:

$$E = mc^2$$

- β^- or β^+ each have a rest mass of 9.109×10^{-31} kg = 0.511 MeV of energy
- To conserve charge and momentum antiparticle, positron must also be created
- Gamma ray energy must be > 1.022 MeV
- Probability of PP increases with energy above 1.022 MeV

Annihilation

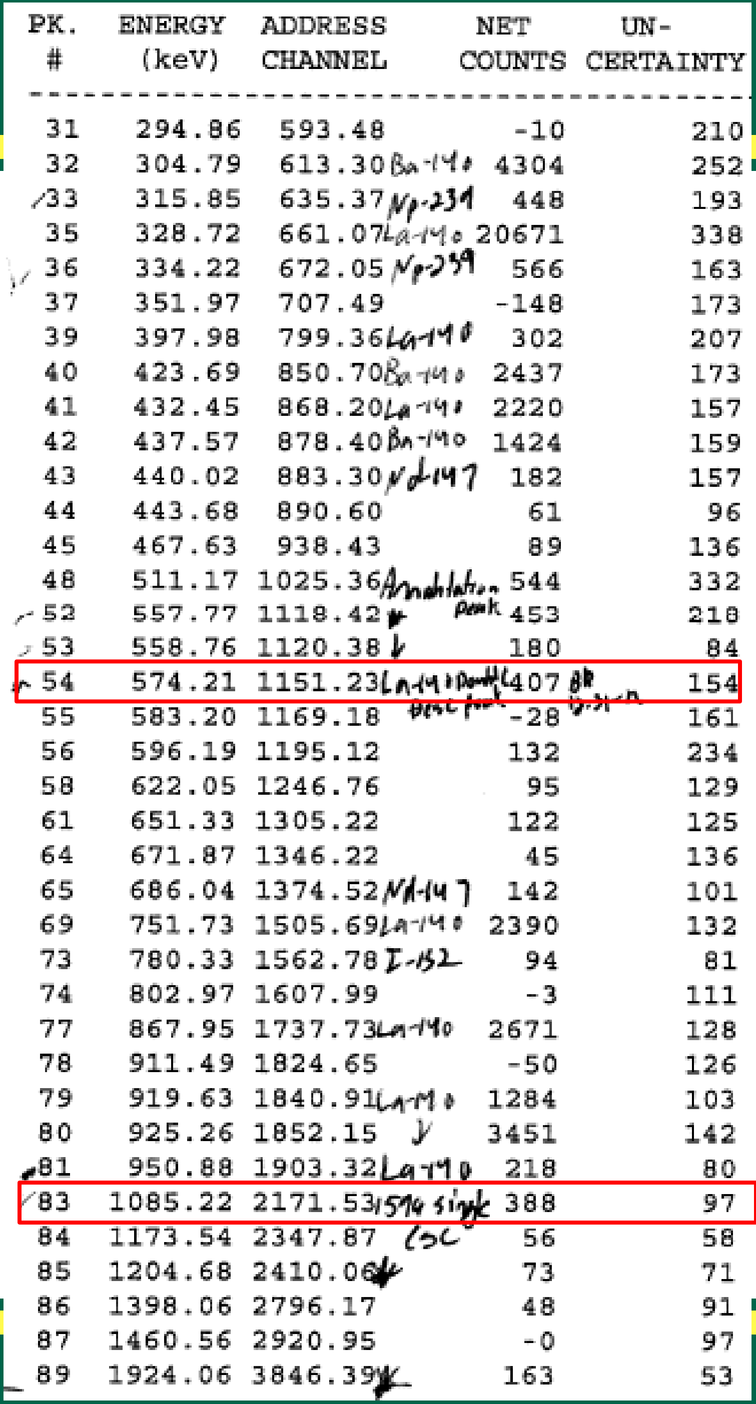


Effect in the Gamma-Ray Spectrum

- If PP occurs in the sample, 511 keV photon may interact with HPGe
- If PP occurs in the detector,
  - 511 keV photon may interact with HPGe
  - Single escape (SE) peak may be observed
  - Double escape (DE) peak maybe observed

Effect of Pair Production

- MFP Sample – 500mL
- Counted for 16 hours
- 1596 keV peak from ^{140}La had 28,465 net counts
- Both the SE and DE peaks were correctly identified
- DE peak will have more counts than the SE peak.

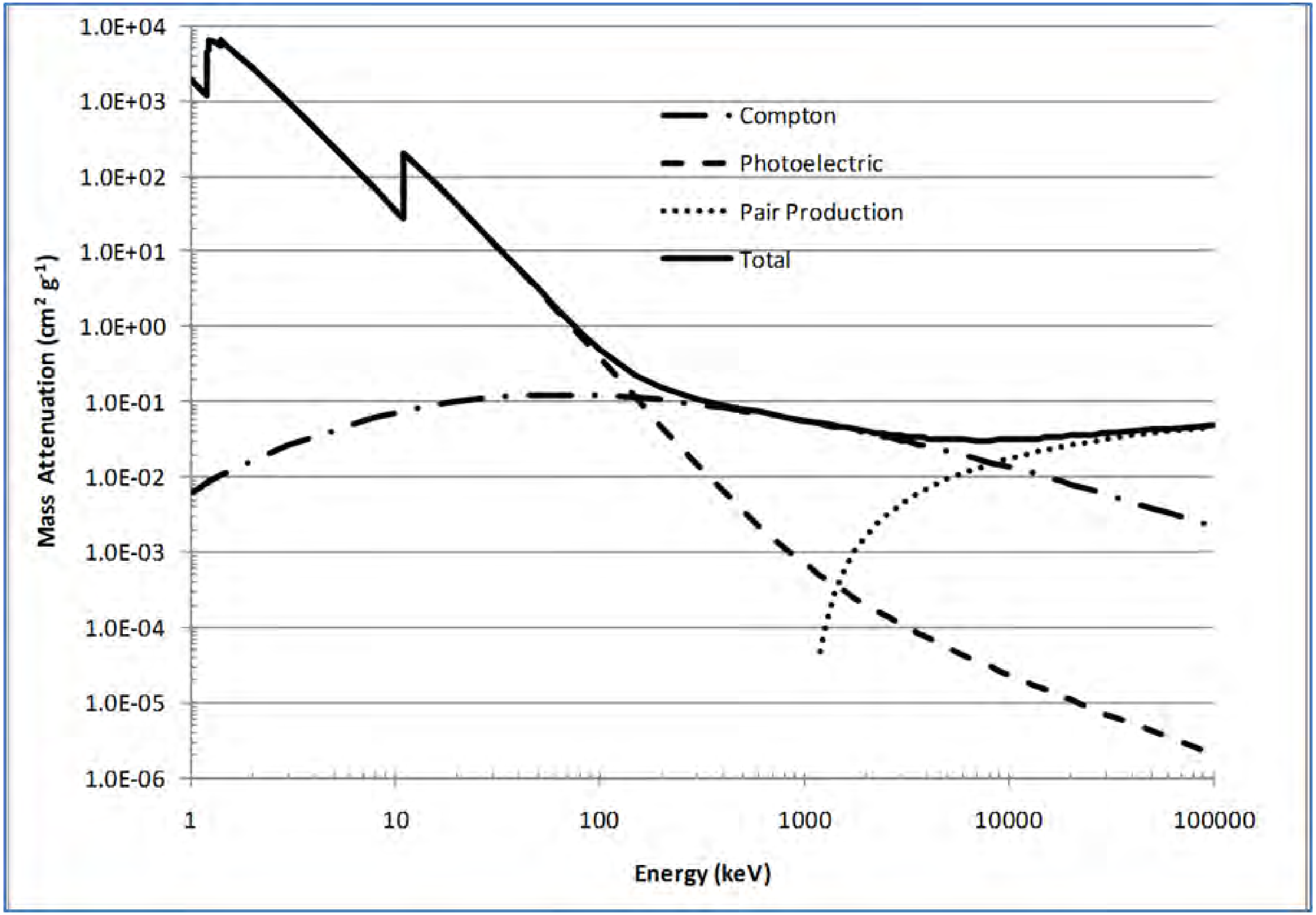


PK. #	ENERGY (keV)	ADDRESS CHANNEL		NET COUNTS	UN-CERTAINTY
31	294.86	593.48		-10	210
32	304.79	613.30	Ba-140	4304	252
33	315.85	635.37	Np-239	448	193
35	328.72	661.07	La-140	20671	338
36	334.22	672.05	Np-239	566	163
37	351.97	707.49		-148	173
39	397.98	799.36	La-140	302	207
40	423.69	850.70	Ba-140	2437	173
41	432.45	868.20	La-140	2220	157
42	437.57	878.40	Ba-140	1424	159
43	440.02	883.30	Nd-147	182	157
44	443.68	890.60		61	96
45	467.63	938.43		89	136
48	511.17	1025.36	Annihilation peak	544	332
52	557.77	1118.42		453	218
53	558.76	1120.38		180	84
54	574.21	1151.23	La-140 Double Escape peak	407	154
55	583.20	1169.18		-28	161
56	596.19	1195.12		132	234
58	622.05	1246.76		95	129
61	651.33	1305.22		122	125
64	671.87	1346.22		45	136
65	686.04	1374.52	Nd-147	142	101
69	751.73	1505.69	La-140	2390	132
73	780.33	1562.78	I-132	94	81
74	802.97	1607.99		-3	111
77	867.95	1737.73	La-140	2671	128
78	911.49	1824.65		-50	126
79	919.63	1840.91	La-140	1284	103
80	925.26	1852.15		3451	142
81	950.88	1903.32	La-140	218	80
83	1085.22	2171.53	1596 single	388	97
84	1173.54	2347.87	(sc	56	58
85	1204.68	2410.06		73	71
86	1398.06	2796.17		48	91
87	1460.56	2920.95		-0	97
89	1924.06	3846.39		163	53

Effect of air Production

- Occasionally there will be photopeaks located in the 1,000 – 2,000 keV range that do not correspond to anything in the library.
- Check to see if any of the identified radionuclides have gamma rays in the 2,000 – 3,000 keV range and look for SE/DE peak possibilities.

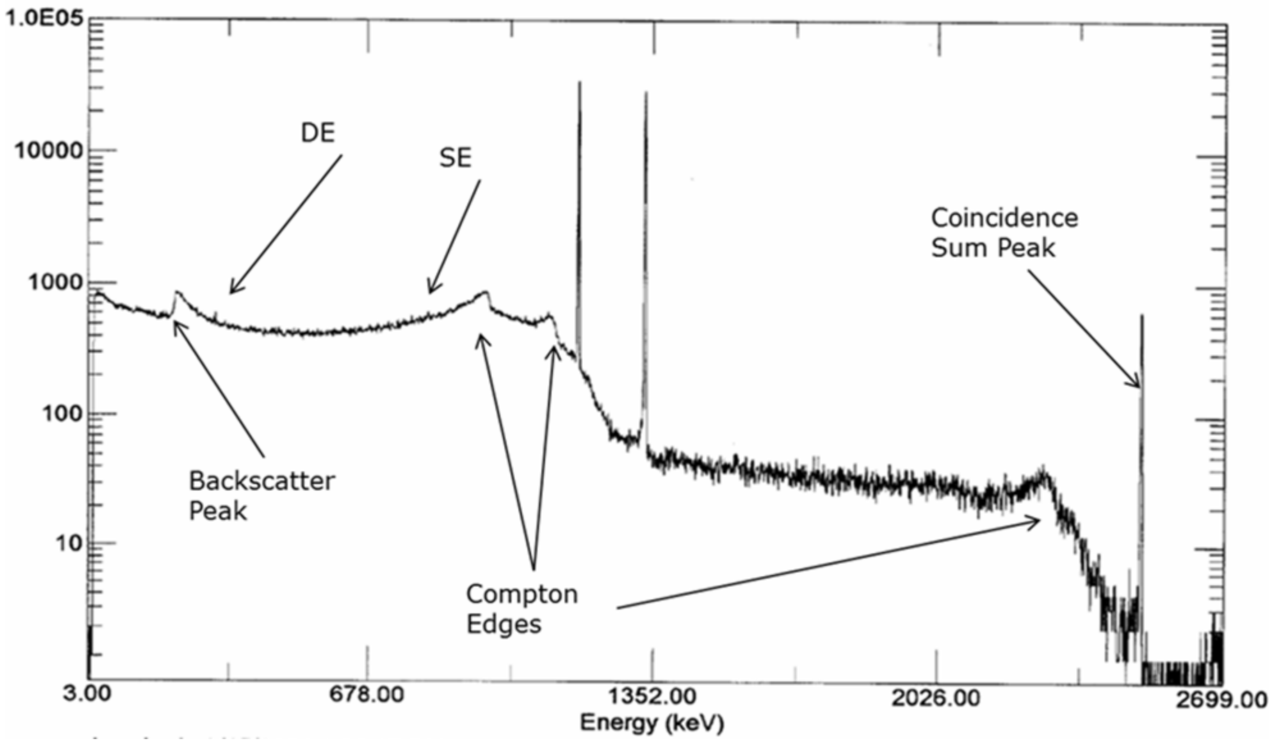
Probability of Interaction



Sum Peaks

- Summing of pulses from gamma-ray interactions in the detector that arrive within the resolving time of the electronics will occur and be registered as the sum of the energies of the gamma rays.
- Summing is generally characterized as random summing or true coincidence (cascade) summing.

Example of Coincidence Summing



Software Functions

What they do.

Why we should select or not select some of them.

What we need to know about them.

What they don't do.

Bob Shannon

Some Software Options

- Peak Search Sensitivity
- Peak Cutoff Sensitivity
- Energy Comparison
- Half-life Ratio Exceeded
- Key Line Designation
- Abundance or Fraction Limit
- Weighted Mean Activity
- Compton and Peak Background Subtract
- Decay Correction
- Decay During Count

Some examples of these on the next few sides

Peak Search Sensitivity (PSS)

- Specifies how large a peak must be relative to Compton continuum to be present in spectrum
  - Usually related to critical value or uncertainty
  - PSS settings commonly range from 1-10 or 1-5
    - Low PSS è high sensitivity for small peaks
    - High PSS è low sensitivity – sees only large peaks
- Algorithm (may be) proprietary - see operator's manual
  - The peak search may be user-specified or fixed (e.g., critical value), driven by the library, or it may a combination of the two

Peak Search Sensitivity (PSS)

- Peaks are located and fitted, and the ROI activity is compared to the Compton continuum.
  - If the observed peak exceeds the PSS, software decides that the peak is present
  - May be supplemented by library search
- If PSS is too low (i.e., sensitivity too high…)
  - False peaks may be identified
    - Small fluctuations in background misidentified as peaks
    - Peaks may be falsely split into multiplets
- If PSS is too high (i.e., sensitivity too low…)
  - Real peaks may ‘disappear’
    - Activity may be greater than the critical level
    - Not available for analysis and/or review

Peak Uncertainty Cutoff

- Peak uncertainty is compared to user-specified cutoff value for uncertainty
  - Remove high uncertainty or "false" peaks from the analysis
  - Remove peaks from unidentified list

PSS/Cutoff Setting Impact Results

- Visually review spectrum - verify that peaks locations and fitting are accurate and reliable
  - Has peak cut-off limit been exceeded (lost peaks)?
  - Are multiple peaks really part of a singlet or are singlet peaks really part of a multiplet?
    - Are PSS settings too low or high?
    - Peaks rejected for calibration issues
      - » peak-shape, Δ-keV?
- Take action to correct problems that impact identification or quantification
  - Disclose deficiency and address limitation on results in the report…

Energy Comparison

- Agreement between observed and library centroid energies one of the criteria that validate peak ID
  - Compare centroid energy found and library values to user-specified tolerance (keV or FWHM)
- Recommendations
  - Keep deltas small – compare to control charts
  - Pay attention to vendor requirements
    - Ortec states, for example, that the same settings be used for calibration and samples and recommends a default setting of ± 0.5 keV (range ± 0.45–0.7 keV), and
  - Sample activity may influence the optimal limit
    - High activity–well-formed peaks smaller delta
    - Low activity–poorly-formed peaks larger delta

Half-Life Ratio Exceeded

- Limits time between reference date and analysis
  - Assumes a radionuclide cannot be present after *x* half-lives
  - Common default is 8-12 half-lives (1/256th-1/4,096th initial activity
- Consider a radionuclide with 2-hour half-life analyzed after 1 week

$$HL_{ratio} = \frac{\Delta T}{t_{1/2}} = \frac{7\text{ days } \times \text{ 2 hours/day}}{\text{2 hours}} = 89\text{ half} - \text{lives}$$

  - Reject result because HL_{ratio} is greater than 12
    - Activity would be 1 / 289 or 1 / 6.2 $x10^{26}$ of initial activity
- Criterion of 8-12 half-lives may exclude valid results!!!
  - Mixed Fission PTs - very real results were not reported
- *Not applicable to parent-progeny relationships*
  - But consider what half-life was used in the library?

Key Line

- Gamma lines that must be present before a radionuclide identification is considered valid
- When building libraries, consider:
  - The ‘key line’ is ideally the highest intensity, interference-free gamma ray for a radionuclide *(could use FOM = efficiency^2 × abundance^2 / background)*
  - Some software packages allow multiple key lines
  - Some software packages automatically designate the first line in a library as key line.
    - If any other line is marked as a key line, there will be 2 key lines!

Key Line (cont.)

- Is the presence or absence of a key line diagnostic?
  - *The most abundant, clean line positive ID (ideal case)*
- Is a radionuclide identification invalid when its most abundant photopeak ***is*** present?
  - *Usually not, but sometimes you need a confirming line*
- Key lines can make radionuclide ID more arbitrary
  - *Key Line* and *Abundance Limit* are redundant tests of radionuclide presence and can work at cross-purposes – do not use them together!
  - This test may behave differently depending on activity levels present and whether you have a short or long library

Key Line? – Oops!

Radionuclide	Half Life	Energy, keV	Abundance, %	Alternate Key Line?	Abundance, %
^{110m}Ag	249 days	657	95.6	884	75.0
^{97}Nb*	1.2 hours	657	98.2	---	---
^{134}I	52.5 minutes	847	96	884	65.1
^{56}Mn	2.57 hours	847	98.85	1810	26.9

*The precursor of ^{97}Nb is ^{97}Zr ($t_{1/2}$ = 16.7 hours) gamma ray at 743 keV is 97 %

Key Line – The ^{60}Co Conundrum

Nuclide	**Co-60**		**Software Decision (present or not)**
Energy (keV)	**1173.2**	**1332.5**	
Abundance ===>	99.85%	99.98%	
No lines identified	▨ O	O	Reject
	O	▨ O	Reject
	▨ O	▨ O	Reject
1 line identified (1173.2 keV)	▨ **X**	O	Present
	X	▨ O	Reject
	▨ **X**	▨ O	Reject
1 line identified (1332.5 keV)	▨ O	**X**	Reject
	O	▨ **X**	Present
	▨ O	▨ **X**	Reject
2 lines identified (1173.2 and 1332.5 keV)	▨ **X**	**X**	Present
	X	▨ **X**	Present
	▨ **X**	▨ **X**	Present

▨	**Key line in library**
O	**Line absent in spectrum**
X	**Line present in spectrum**

Note: You may not be able to disable the key-line test!

Abundance (Fraction) Limit (AL)

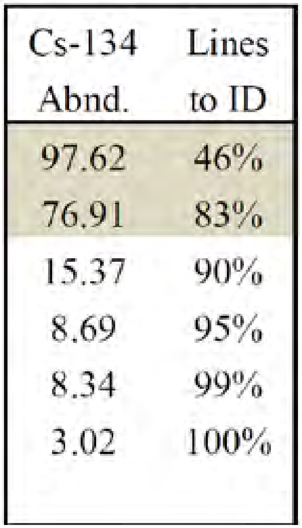
- Tests to see if there is sufficient photopeak activity to conclude that a radionuclide has been identified
  - The AL is the ratio of the summed abundance of gamma rays identified for the radionuclide relative to all lines in the library for that radionuclide
  - If this ratio does not exceed the user-specified AL, the identification is rejected and the gamma rays are moved to an unidentified or rejected lines report
- Intended to perform essentially the same task as the key-line test

Abundance Limit - Concerns

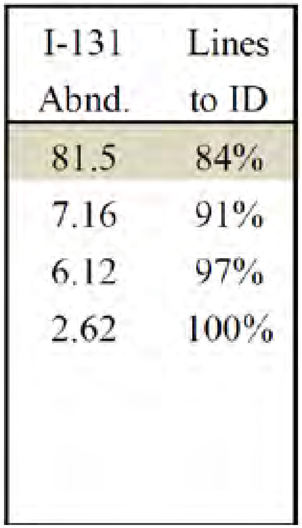
- Can be unavoidably arbitrary
  - Less discriminating than key line test - a single limit is generally applied to all nuclides in library although abundances vary by radionuclide
  - Generally recommend disabling this test
    - Works at cross purposes with key-line test
    - Different results obtained for long versus short libraries, or for low versus high activity samples, or for subtle differences in limit applied

Abundance Limit - Analysis of Miner's Lettuce after Fukushima

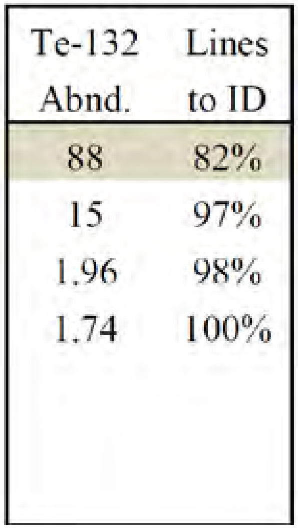
- The abundance limit was set to 75%
- The right column in each box tracks the cumulative abundance as more lines are detected
- Criteria for identification are arbitrary (or worse)
  - For ^{131}I, only one photopeak is needed
  - ^{136}Cs will not be identified until three lines are present
    - One of these lines has much lower abundance



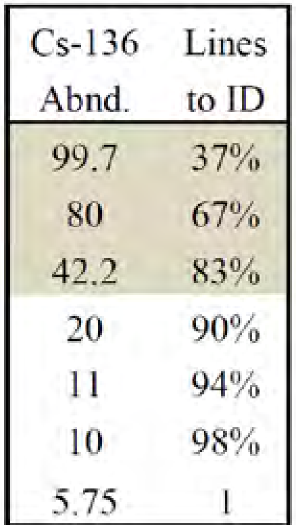
Cs-134 Abnd.	Lines to ID
97.62	46%
76.91	83%
15.37	90%
8.69	95%
8.34	99%
3.02	100%



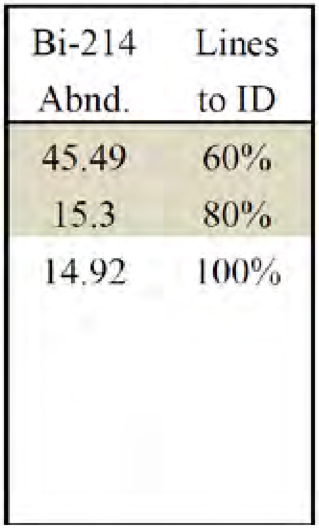
I-131 Abnd.	Lines to ID
81.5	84%
7.16	91%
6.12	97%
2.62	100%



Te-132 Abnd.	Lines to ID
88	82%
15	97%
1.96	98%
1.74	100%



Cs-136 Abnd.	Lines to ID
99.7	37%
80	67%
42.2	83%
20	90%
11	94%
10	98%
5.75	1



Bi-214 Abnd.	Lines to ID
45.49	60%
15.3	80%
14.92	100%

Weighted Mean Activity

Two types

- Weighted by abundances of found gamma rays
- Weighted by uncertainty of found gamma rays

In both cases:

Review the range of values for the gamma rays used for analysis

Equations for Weighted Mean Activity

Uncertainty-Weighted Mean Activity and Uncertainty

$$C_{avg} = \frac{\sum_{i=1}^{n}(C_i/\sigma_{C_i}^2)}{\sum_{i=1}^{n}\frac{1}{\sigma_{C_i}^2}} \qquad \sigma_{Cavg} = \sqrt{\frac{1}{\sum_{i=1}^{n}\frac{1}{\sigma_{C_i}^2}}}$$

Abundance-Weighted Mean Activity and Uncertainty

$$C_{avg} = \frac{\sum_{i=1}^{n} C_i \times I_{C_i}}{\sum_{i=1}^{n} I_{C_i}} \qquad \sigma_{Cavg} = \frac{\sum_{i=1}^{n}(\sigma_{C_i} \times I_i)}{\sum_{i=1}^{n} I_i}$$

Where:

C_{avg} *is average activity*

σ_{Cavg} *is the uncertainty of* C_{avg}

C_i *is the activity of the* i^{th} *qualifying peak*

σ_i *is the uncertainty of the* i^{th} *qualifying peak*

I_{C_i} *is the abundance of the* i^{th} *qualifying peak*

n is the number of peaks averaged

Wtd. Mean - More Data is Not Always Better

What happens as fewer lines are averaged?

	Activity (pCi)	Uncertainty (pCi, k=1)	Abundance
Line 1	10	1	0.99
Line 2	8	1.5	0.8
Line 3	15	2.5	0.7
Line 4	16	5	0.25
Line 5	1000	499	0.01

	Arithmetic mean	Uncertainty wtd. mean	Abundance wtd. mean
Mean	210	10.09	14.8
Stnd Unc (k=1)	442	0.78	3.7

	Activity (pCi)	Uncertainty (pCi, k=1)	Abundance
Line 1	10	1	0.99
Line 2	8	1.5	0.8
Line 3	15	2.5	0.7
Line 4	16	5	0.25

	Arithmetic mean	Uncertainty wtd. mean	Abundance wtd. mean
Mean	12.3	10.09	11.2
Stnd Unc (k=1)	3.9	0.78	1.9

	Activity (pCi)	Uncertainty (pCi, k=1)	Abundance
Line 1	10	1	0.99
Line 2	8	1.5	0.8
Line 3	15	2.5	0.7

	Arithmetic mean	Uncertainty wtd. mean	Abundance wtd. mean
Mean	11.0	9.94	10.8
Stnd Unc (k=1)	3.6	0.79	1.6

	Activity (pCi)	Uncertainty (pCi, k=1)	Abundance
Line 1	10.00	1.00	0.99
Line 2	8.00	1.50	0.80

	Arithmetic mean	Uncertainty wtd. mean	Abundance wt. mean
Mean	9.0	9.38	9.1
Stnd Unc (k=1)	1.4	0.83	1.2

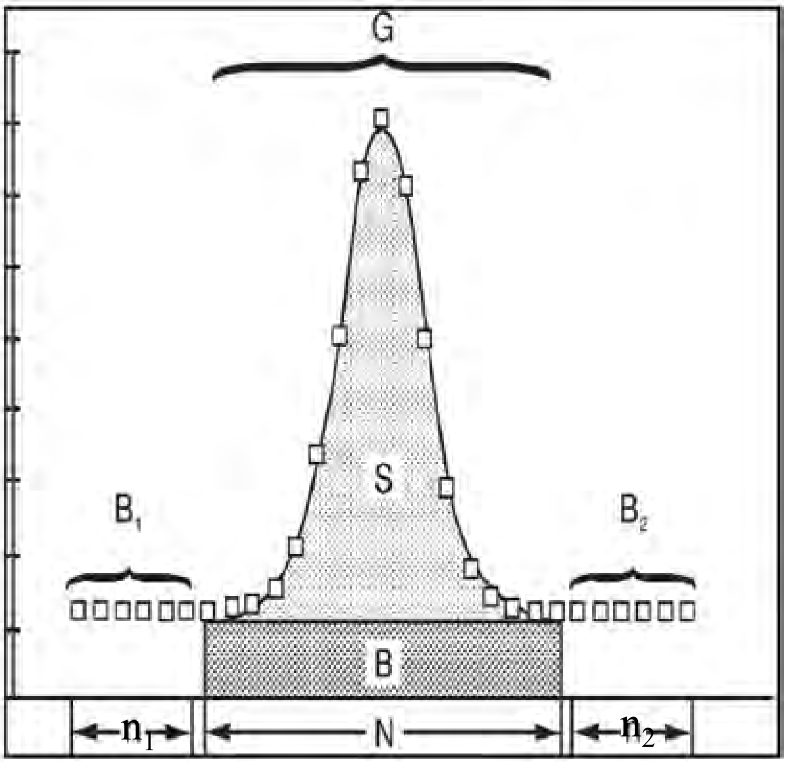
Compton Background – Net Peak Activity

A very simplified geometric method for determining net peak area, S, for a non-multiplet peak

Where:

G is the gross peak area
B - peak background (counts)
N - number of channels in the peak ROI
n_1 - continuum channels on right side
n_2 - continuum channels on each side
B_1 sum of counts in continuum region to left of peak
B_2 sum of counts in continuum region to right of peak

$$\mathbf{S} = \mathrm{G} - \mathrm{B} = \mathrm{G} - \left[\frac{\left(\frac{\mathbf{B_1}}{\mathbf{n_1}} + \frac{\mathbf{B_2}}{\mathbf{n_2}}\right)}{2} \times \mathbf{N}\right]$$



The biggest challenge is determining B_1 and B_2 for peaks ranging from small to large

- How many channels do you average? One setting for the spectrum, or an algorithm that picks and optimal setting? Careful review needed ? (yes…) Interactive fitting ? (probably)
- When is another peak too close? (*Let's save multiplets and more advanced peak fitting topics for another day…)*

Peak Background Subtraction (PBS)

- "Peak Background" - Full-energy peaks from radionuclides in the shield and detector materials
  - Naturally-occurring radionuclides, e.g. ^{40}K, ^{235}U, radium/progeny
  - Other radionuclides present (if detector has been contaminated)
- General approach (specific approaches may vary)
  - Analyze the background spectrum
    - For small samples count an empty chamber background
    - For media/sample containers that contain analyte, or large samples (e.g., 4-L Marinelli) that shield detector, collect background with surrogate sample in place
  - Count duration should be (much) longer than sample counts
  - Use software to subtract activity from each peak in sample spectra
- Monitor and control background and blanks carefully!
- No PBS needed if background doesn't overlap radionuclides of concern. It only adds uncertainty to the measurement.

Gamma Spectrometry Decay Corrections

- It is an (often unwritten) industry default that results should be decay corrected to collection date - or perhaps earlier (e.g., event date).
- Most gamma spectrometry software corrections for decay use the following equation which assumes that the radionuclide activity is unsupported:

$$A_0 = \frac{A_1}{e^{-\lambda \Delta t}}$$

Where

A_0 is activity corrected for unsupported decay to the decay reference date

A_1 is activity at time of count

λ is the decay constant ($= 0.693 / t_{1/2}$)

Δt is the time elapsed between the decay reference date (e.g., collection) and the sample count

Some software packages provide support for more complex parent-progeny decay corrections. Beyond properly configuring the software, it is the responsibility of the user to ensure that the considerations about equilibrium and sample integrity discussed here have been met!

Decay Correction for Supported Activity

- Are the radionuclides unsupported?
  - If unsupported, your software is set to go…
- For parent-progeny pairs,
  - Were they in equilibrium at time of the count?
    - If you have results for both radionuclides, verify the ratio!
  - Were they in equilibrium at the time of collection?
    - Was there enough time for the pair to reach equilibrium before collection? Perhaps, perhaps not…
    - Do both parent and progeny behave identically in the environment prior to sampling? (not generally)
    - You may have a special case (e.g., highly refractory or insoluble analytes)?

Decay Correction for Supported Activity

- Progeny decay is controlled by parent half-life as long as the sample is in equilibrium
  - We can therefore use the equations for unsupported decay in gamma software by replacing the progeny half-life in the library with the parent half-life
  - You cannot correct to a date before equilibrium was reached (usually collection/preservation)
- This is done quite routinely but are the ground rules on equilibrium being considered/satisfied?

Decay Corrections – Know the Limitations!

- If a pair is in equilibrium at the count, but you do not know if it was in equilibrium at collection (or other reference time),

STOP! You may not be able to defensibly correct for decay!!

- Inform the customer that it is mathematically impossible/incorrect to perform decay correction
  - If the customer asks you to make an assumption and you agree, make sure you qualify all affected results, document and disclose all assumptions and their impact on results

Manual Decay Corrections

- If the sample is not in equilibrium at the time of the count, use the Bateman equation

$$A_d^1 = A_d^0 \mathrm{e}^{-\lambda_d \Delta \mathrm{t}} + A_p^0 \left(\frac{\lambda_d}{\lambda_d - \lambda_p} \right) \left(\mathrm{e}^{-\lambda_p \Delta \mathrm{t}} - \mathrm{e}^{-\lambda_d \Delta \mathrm{t}} \right)$$

(remember this equation – it can be rearranged to solve for A_d^1

see the guide for more details)

- If not, we cannot usually correct to a point in time before sample integrity was preserved
  - How can we know there is no fractionation?

Decay During Counting (DDC) Correction

- A software feature that may be selected is to correct for decay during counting
  - Important for long count times when radionuclides undergo ‘significant’ decay during the count

$$C_f = \frac{\lambda t_c}{(1-e^{-\lambda t_c})}$$

Where:

C_f is the correction factor (DDC, a dimensionless quantity)
λ is the decay constant for a particular radionuclide (s^{-1})
t_c is the live time of the analysis (s)

- What is ‘significant’?

Detection Equations, Validation and Examples

Detection Equations

- Many different terms are used for "detection"
  - MDA, MDC, LLD, L_c
- Each term has a different equation
- Each equation different assumptions regarding confidence interval or tolerable error rate
- Some software packages have eight (8) or more different options

Detection Factors

- Several factors impact detection
  - Detector efficiency for the gamma ray of interest
  - Abundance of the gamma ray
  - Sample size
  - Count time
  - Background
  - Others…
- The real question *may be*---
  - How sure do we want to be that the net sample counts are greater than the average background counts corresponding to zero?

Critical Level Concentration

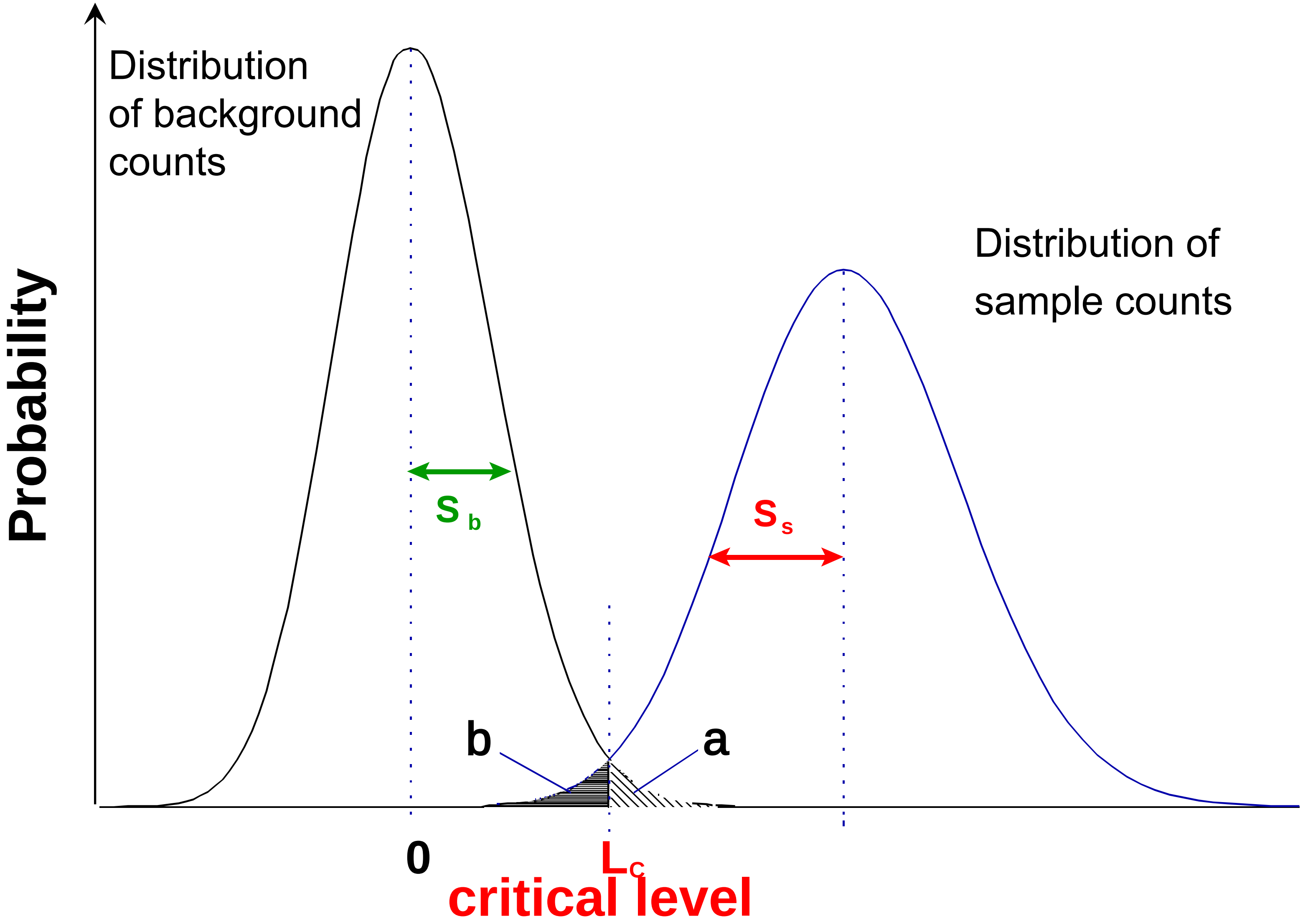
"The minimum measured value (e.g. of the instrument signal or the *analyte* concentration) required to give confidence that a positive (nonzero) amount of *analyte* is present in the material analyzed"

$$L_c = 2.33 \times \frac{\sqrt{B}}{t \times \varepsilon \times A \times V}$$

Where:

B are the background counts
t is the count time
ε is the detector efficiency at the gamma-ray energy
V is the sample volume or mass
A is the gamma ray abundance

This Assumes that Measured Results Follow…



Minimum Detectable Amount

The minimum detectable value of the amount of analyte in a sample. Same concept as the *minimum detectable concentration* but related to the quantity (activity) of a *radionuclide* rather than the concentration of a *radionuclide*, and the equation has a different basis.

$$MDA = \frac{A + \sqrt{B + C \times counts}}{Live\ time \times (efficiency \times yield)}$$

A, B and C are constants used to add background counts preventing a calculation of zero uncertainty.

C, often selected as 21.7, is statistically derived from the tolerable error rate of $Z_{1-\alpha}^2$ from the *critical concentration formula* at 5 % tolerable error rate

Minimum Detectable Concentration

The smallest ***a priori*** radionuclide concentration for which there is:

> 5% probability of obtaining a result below the critical level (i.e., 5% probability of falsely concluding that the result represents a blank)
>
> — *and simultaneously* —
>
> 95% probability of obtaining a result greater than the critical value (i.e., 95% probability of concluding that there is activity in the sample and it is not a blank)

$$\mathrm{MDC} = \frac{\mathrm{L_D} \times \mathrm{C_f}}{\mathrm{t_c} \times \varepsilon' \times \mathrm{A} \times \mathrm{V} \times \mathrm{k_w} \times \mathrm{k_x} \times \mathrm{F} \times \mathrm{U_f}}$$

L_D is the twice critical level plus the square of the tolerable error rate,

$$L_D = 2 \times L_C + z_{1-\alpha}^2$$

ε' is the attenuation corrected efficiency

F is the sample mass/volume conversion factor

V is the volume or mass

A is the abundance factor for the gamma ray

C_f is the correction for decay during counting

k_w is the decay correction from the start of the count time to the time the sample was obtained.

t_c is the clock time

U_f is the unit conversion factor from Bq to the desired units (e.g., pCi)

k_x is the correction for decay during sample accumulation time.

Lower Limit of Detection

This equation determines an ***a priori*** limit of detection based on optimal characteristics of the detection system and the sample.

$$LLD, \mu Ci/mL = \frac{4.66 \times \sigma_b}{(3.7 \times 10^4 \times E \times V \times Y \times e^{-\lambda \Delta t})}$$

Where:

σ_b = standard deviation of the background
E = detector efficiency
V = volume of sample in mL
Y = Chemical yield (=1 for gamma spec)
Δt = elapsed time between sampling and counting

Which Equation?

Four different detection equations four different results for detection. Which one is correct?

- The most commonly used detection equation, the MDC, yields a value that is about twice the value of the critical level concentration.
- Also note that increasing the count time by a factor of four only reduces the detection limit by a factor of two…

You have the ability to select the equation you need to use. And remember sometimes the detection equation used may be governed by *regulation* or *contract*.

Detection Equation Calculations

			Activity at beginning of Count interval, pCi/L			
	Bg, cps	**Fractional Efficiency**	**Lc**	**MDA**	**LLD**	**MDC**
14400 sec	0.01	0.01	6.2	10.5	12.3	12.9
(4 Hours)	0.05	0.01	13.8	23.5	27.6	28.1
	0.1	0.01	19.5	33.3	39.0	39.5
	1	0.11	5.6	9.6	11.2	11.2
	10	0.21	9.3	15.8	18.6	18.6
	100	0.31	19.9	33.9	39.8	39.7
3600 sec	0.01	0.01	12.3	21.0	24.7	27.0
(1 Hour)	0.05	0.01	27.6	47.0	55.2	57.5
	0.1	0.01	39.0	66.5	78.0	80.3
	1	0.11	11.2	19.1	22.4	22.6
	10	0.21	18.6	31.7	37.1	37.2
	100	0.31	39.8	67.9	79.6	79.5

Note that the value for the constants in the MDA equation used were A=0, B=0 and C=5.43. This was done to allow the numerator to align with the L_D value of twice the L_C. If the usual value of 21.7 was used the MDA value would have been a factor of about 2 *higher*

VERIFICATION AND VALIDATION

WHO PERFORMS IT AND HOW?

What are …

- Numbers?
- Results?
- Data?

Who Does the V&V?

- Both the laboratory and the client have responsibilities
  - Data reported by the laboratory should “make sense” based on the type of sample and circumstances
  - Client should critically review the results and associated data ensuring what they asked for has been done
- There will be some overlap in these responsibilities

Verification

- First step is verification
- For verification process all of the required *data* necessary to calculate the sample results must be present.
- The checklist used should be in the form of a "yes" or "no" response.

How is it Done?

- *Some* of the questions that need answers (Y/N) are:

Is all of the sample input data identified correctly on the gamma Spectrometry printout?
Has the correct library been used for this sample analysis?
Has the radioactive sample-holding time been exceeded?
Are all identified radionuclides included based on half-life?
Have appropriate members of decay chains been identified?
Are proper half-lives used for radionuclides in parent-progeny relationships?
Are all the FWHM used to calculate activity concentrations at the approximate value for the gamma-ray energy?
Are all identified radionuclides expected or probable?

Validation

- Ensures that all of the required inputs to validate the data are present based on the verification process
- Examines the analytical *data* to ensure that it supports the use of the results for defensible actions.

Validation

All verification report inputs satisfactory ?	Y___ N___
All QC analyses Satisfactory?	Y___ N___
Have all software preset functions been optimized based on the client requirements and sample history to identify the radionuclides present?	Y___ N___
Client Requirements Met?	Y___ N___
Sensitivity Factor:	
Half-life ratio:	
Energy Difference:	
Abundance factor:	
Key line:	
Weighted Mean:	
Have all unknown gamma-ray lines with a cps 1-sigma uncertainty less than 50 % been identified?___	Y___ N___
List all unidentified gamma rays: ____ ____	
Have all radionuclide activity concentrations requested by the client been reported?	

Examples

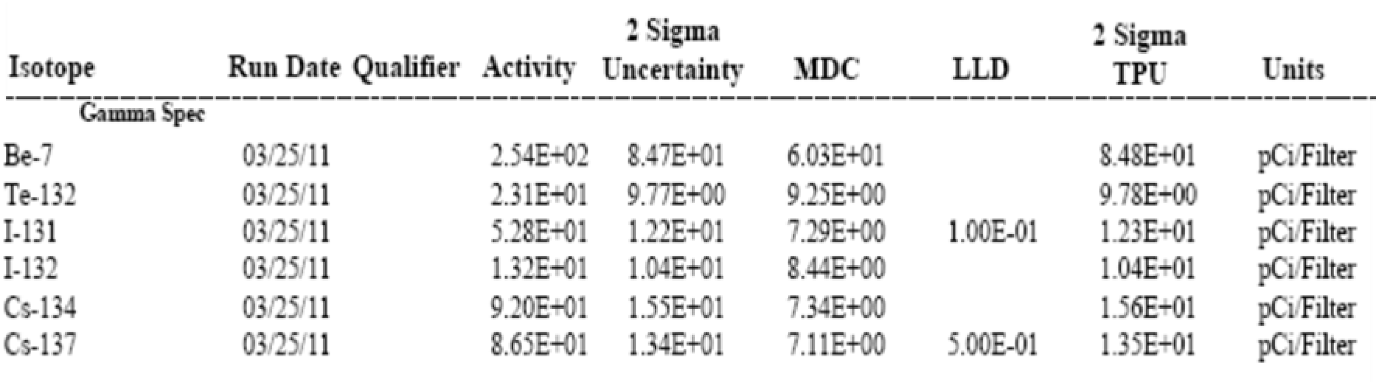
- The next few slides are examples from actual reported results
- In each example, the questions that should have been asked/answered by the reporting laboratory, were not.

Do These Results “Make Sense”?

Results from the Irradiated Uranium PT

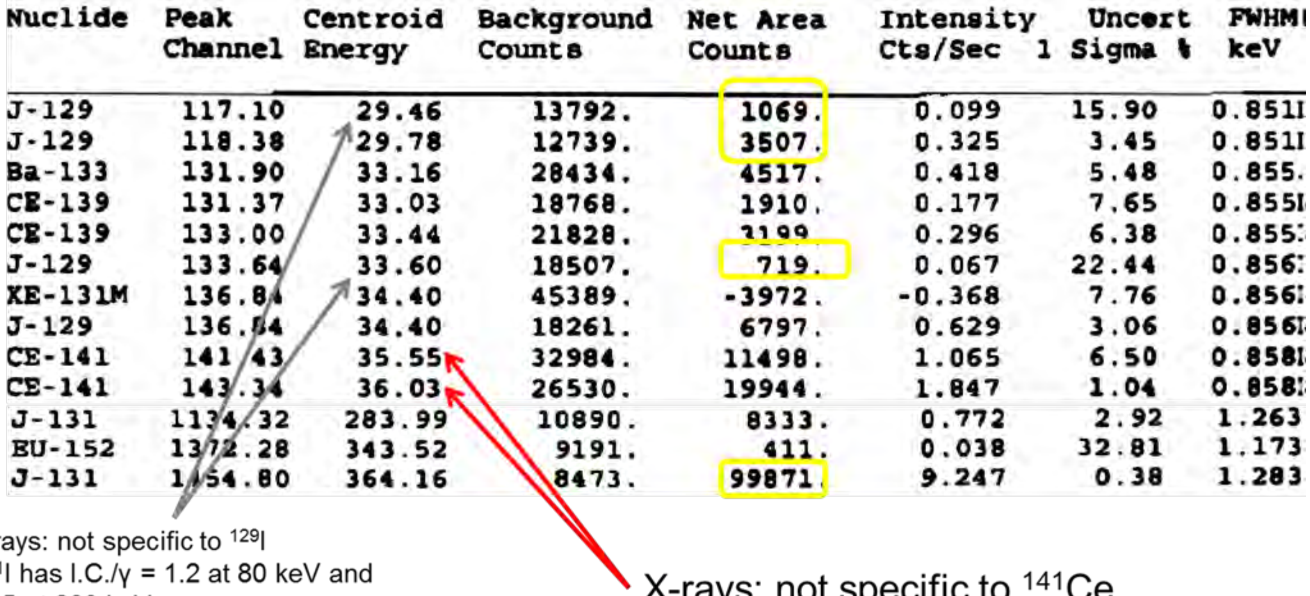
Laboratory		Activity Concentration, pCi/L		Measured Ratio/Theoretical (progeny/parent)	Activity Concentration, pCi/L		Measured Ratio/Theoretical (progeny/parent)
		^{140}La	^{140}Ba		^{99m}Tc	^{99}Mo	
1	Activity[1] at the start of the counting interval	$1.98\text{x}10^{3}$	$1.88\text{x}10^{3}$	1.05/ 1.13	---	---	---
	Corrected for decay back to time of collection	$2.07\text{x}10^{5}$	$3.46\text{x}10^{3}$	59/1.00	**$1.0\text{x}10^{26}$**	$5.03\text{x}10^{7}$	**$2\text{x}10^{22}$**/0.96
2	Activity[1] at the start of the counting interval	---	---	---	---	---	---
	Corrected for decay back to time of collection	$2.49\text{x}10^{6}$	$8.97\text{x}10^{3}$	$2.78\text{x}10^{2}$ /1.00	**$4.17\text{x}10^{19}$**	$2.59\text{x}10^{3}$	$1.6\text{x}10^{16}$/0.96

Radionuclide Activity Ratios



Isotope	Run Date	Qualifier	Activity	2 Sigma Uncertainty	MDC	LLD	2 Sigma TPU	Units
Gamma Spec								
Be-7	03/25/11		2.54E+02	8.47E+01	6.03E+01		8.48E+01	pCi/Filter
Te-132	03/25/11		2.31E+01	9.77E+00	9.25E+00		9.78E+00	pCi/Filter
I-131	03/25/11		5.28E+01	1.22E+01	7.29E+00	1.00E-01	1.23E+01	pCi/Filter
I-132	03/25/11		1.32E+01	1.04E+01	8.44E+00		1.04E+01	pCi/Filter
Cs-134	03/25/11		9.20E+01	1.55E+01	7.34E+00		1.56E+01	pCi/Filter
Cs-137	03/25/11		8.65E+01	1.34E+01	7.11E+00	5.00E-01	1.35E+01	pCi/Filter

- This was a dry deposition sample post-Fukushima
- The time period between sampling and gamma spectrometry analysis was approximately 3 days.
- The ratio of ^{132}I/^{132}Te calculated from the above data is 0.57.
- With a half-life of 2.3 hours, there was ample time for the ^{132}I to reach equilibrium prior to the analysis. The activity ratio at equilibrium is 1.03
- This is a sample preservation issue



Nuclide	Peak Channel	Centroid Energy	Background Counts	Net Area Counts	Intensity Cts/Sec	Uncert 1 Sigma %	FWHM keV
J-129	117.10	29.46	13792.	1069.	0.099	15.90	0.851
J-129	118.38	29.78	12739.	3507.	0.325	3.45	0.851
Ba-133	131.90	33.16	28434.	4517.	0.418	5.48	0.855
CE-139	131.37	33.03	18768.	1910.	0.177	7.65	0.855
CE-139	133.00	33.44	21828.	3199.	0.296	6.38	0.855
J-129	133.64	33.60	18507.	719.	0.067	22.44	0.856
XE-131M	136.84	34.40	45389.	-3972.	-0.368	7.76	0.856
J-129	136.84	34.40	18261.	6797.	0.629	3.06	0.856
CE-141	141.43	35.55	32984.	11498.	1.065	6.50	0.858
CE-141	143.34	36.03	26530.	19944.	1.847	1.04	0.858
J-131	1134.32	283.99	10890.	8333.	0.772	2.92	1.263
EU-152	1372.28	343.52	9191.	411.	0.038	32.81	1.173
J-131	1454.80	364.16	8473.	99871.	9.247	0.38	1.283

X-rays: not specific to ^{129}I
(^{131}I has I.C./γ = 1.2 at 80 keV and
0.05 at 283 keV

X-rays: not specific to ^{141}Ce

- X-rays of iodine were used to determine ^{129}I
- X-rays of cerium were used for ^{141}Ce analysis instead of using the 145 keV gamma ray (which was not identified but present)
- X-rays of Ba were used to determine Ba-133 (which was not present but Ba-140 was)
- X-rays of I, Ba or Ce are representative of *any* isotope of that element, they are not useful for identification or quantification of any specific isotope.

HOW…?

WHY…?