

**RADIOLOGICAL FALSE POSITIVES IN ENVIRONMENTAL SOIL AND GROUNDWATER DATA
FROM COMMERCIAL LABORATORIES**

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ABSTRACT

Laboratory identification of radionuclides at environmental concentrations can easily be mistaken, because many energy interferences (coincident or overlapping spectral peaks) are possible. Conventional laboratory quality control measurements are typically not designed to test interferences found in real samples. In order to evaluate the occurrence of radiological false positives in environmental soil and groundwater samples collected at the Savannah River Site, instrument printouts, calibration records, and procedure manuals were examined between 1997 and 2001 at five commercial radiological laboratories.

False positives of many radionuclides were found to be routinely reported at all five laboratories; causes vary. Magnitudes were generally between 0.1 and 3 pCi/g in soils, and between 2 and 40 pCi/L in groundwater, within the range of possible concern to regulators. The frequency of false positives varied, but for several nuclides listed below, nearly every detection reported in SRS environmental samples during the study period was judged to be false.

Gamma spectroscopy: Low-level false positives of Mn-54, Zr-95, Eu-155, and Np-239 were reported in many soil samples from four laboratories, due to interference from naturally occurring Tl-208, Pb-212, and Ac-228. There were two causes. First, laboratories did not include low abundance (<2%) peaks of Tl-208, Pb-212, and Ac-228 in the libraries used by instrument software for interference correction. Second, even when instrument software rejected the identifications, incorrectly identified nuclides were still often reported as detected, because some labs' data management systems were not able to distinguish between software-accepted nuclides and software-rejected nuclides. Magnitudes of these false positives are usually below 1 pCi/g.

Alpha spectroscopy: Incomplete chemical separation and breakthrough of natural radionuclides and/or daughters of laboratory tracers generate false positives in soils up to about 5 pCi/g. Examples include natural Th-228 causing false positives of Am-241 and Pu-238; natural U-234 being mistaken for Np-237; and natural Ra-224 generating false positives of Cm-243/244. Peak taildown of tracers or other nuclides into neighboring peak windows can also generate false positives in both soils and groundwater. Examples include taildown of Th-229 tracer into the Th-230 spectral window, and U-234 taildown causing false positives of U-235.

Liquid Scintillation: Incomplete chemical separation may generate false positives of virtually any Liquid Scintillation nuclide. High tritium content in Savannah River Site groundwater causes false positives of C-14. Actinides produce false positives of Pm-147.

Most false positives in alpha spectroscopy and liquid scintillation counting at commercial labs are due to incomplete separation of the target nuclide from interferors. However, quality control measurements such as matrix spikes and chemical yield are often unable to identify cases where interfering nuclides break through into the final preparation. In addition, laboratory personnel often fail to manually interpret sample spectra, and thus do not notice peak interference when it occurs. In fact, some laboratories are unable to produce energy spectra for liquid scintillation or alpha spectroscopy, making recognition of peak interference virtually impossible.

Gamma spectroscopy of environmental samples usually does not involve chemical separation, so peak interference may occur in every sample. Interference correction software appears to be ineffective at the concentrations seen in

environmental samples. At all labs, careful manual review of printouts appeared to be lacking when the study was performed. Some labs have improved their data review processes since then.

INTRODUCTION

Characterization of environmental waste sites for radionuclides depends upon many radiological analyses of soil and groundwater samples, often performed at commercial laboratories. Data user confidence in the quality of commercial laboratory analyses is relatively high, because laboratories are held to disciplined conduct of operations by auditing and certifying organizations, and because the laboratories follow detailed and laborious Quality Assurance / Quality Control (QA/QC) programs. Laboratories participate in various Performance Evaluation Programs, usually successfully. Finally, much laboratory data undergoes independent validation by customers.

Many things can go wrong with a laboratory analysis to generate an inaccurate result; the layers of QA/QC and data validation are intended to monitor and prevent these occurrences. However, despite multiple levels of scrutiny, not all possible problems are dealt with adequately. QA/QC programs, Performance Evaluation Programs, and EPA data validation guidance are good at addressing instrument energy calibration, instrument efficiency, counting statistics, instrument precision, chemical yield, and contamination of samples or detectors. On the other hand, two important issues are often insufficiently addressed for environmental samples: (1) peak interference/overlap, and (2) incomplete chemical separation (breakthrough). The result of these programmatic blind spots is that false positives of several nuclides are routinely produced at some commercial laboratories, and that there is a lack of awareness among both laboratory and validation personnel regarding the possibility of false positives in environmental data.

DISCOVERY OF FALSE POSITIVES IN ENVIRONMENTAL DATA AT SAVANNAH RIVER SITE

The Savannah River Site (SRS) obtains about 40,000 radiological analyses of soil and groundwater per year. At any given time, two or three different commercial laboratories are employed; about five have been used since 1996. In the late 1990's, apparent false positives of Eu-155 were seen in a non-radiological waste unit, the Central Shops Burning Rubble Pits. This waste unit received construction debris and excessed equipment in the 1950s, and did not have a known history of radiological contamination. Eighty-eight (88) soil samples were collected down to depths of 25 feet. Cs-137, the most abundant radiological soil contaminant at SRS, was detected in 38 samples, with an average concentration of 0.03 pCi/g, consistent with local background. Fission yield calculations indicate that the Eu-155/Cs-137 activity ratio should be about 0.01, suggesting an average Eu-155 concentration of 0.0003 pCi/g, below instrument detection. However, Eu-155 was detected in 76 samples, twice as many as Cs-137, with an average concentration of 0.08 pCi/g, more than twice the value for Cs-137. This same pattern of unsupported Eu-155 detects was found in other presumed-clean waste units. In order to investigate the accuracy of these unexpected detections of Eu-155, the laboratory's analytical method, gamma spectroscopy, was reviewed carefully. Following findings of false positives in gamma spectroscopy, other common laboratory methods were reviewed carefully as well. Results are presented below.

FALSE POSITIVES IN GAMMA SPECTROSCOPY

Gamma spectroscopy is used for nuclides in both soil and groundwater. Its advantages are: (1) ability to quantitate many nuclides simultaneously, and (2) it does not require chemical separation of target nuclides from the sample. An energy spectrum of gamma-ray peaks is produced during sample counting. Nuclide identification is made by comparing measured gamma-ray energies with the instrument's software library.

The absence of chemical separation means that all nuclides present in the sample will contribute gamma rays to the detector, and if two nuclides happen to have similar gamma-ray energies, the detector may report a falsely high result for one or both of them. If one of these nuclides with coincident gamma-ray energies is naturally occurring, and the other is anthropogenic, the gamma spectrometer may report a false positive of the anthropogenic nuclide. This may make a clean site appear to be contaminated, or hazardous waste appear to be mixed waste.

Laboratory analysts are aware of this phenomenon in general, and instrument software is capable of correcting some interferences. Unfortunately, at low concentrations typical of environmental soils, analytical uncertainty is often too

high to allow effective use of interference correction software. Interference suppression depends upon awareness by laboratory personnel. However, several common naturally-occurring interfering nuclides (Ac-228, Tl-208, Pb-212, Bi-212, Pb-214, Pa-234) exhibit many gamma-ray peak energies. For example, 70 distinct gamma-ray peaks are known for Ac-228. Laboratory personnel, in general, are familiar only with the most intense (“most abundant”) peaks of Ac-228 and other natural nuclides.

The nuclide which triggered false positive concerns at SRS was Eu-155. It exhibits detectable gamma-ray peaks at two energies, 86.5 keV and 105.3 keV. Both peaks are close to minor peaks of naturally-occurring radionuclides at 87.2 and 105.0 keV (see table below). Upon review of raw data and conversations with laboratory personnel, it was found that low-abundance gamma-rays from Pb-212 and Ac-228 were the cause of the Eu-155 false positives. Analysts were not aware of the possibility of misidentifying Ac-228 as Eu-155; the 105.0 keV Ac-228 peak, being a minor peak, was not programmed into the instrument software’s peak library. Discussions at two other commercial laboratories found lack of awareness of this interference at both facilities, as recently as 2001.

Other common gamma spectroscopy false positives which were found to affect SRS soils are shown in Table 1. In most cases, a naturally-occurring nuclide, or combination of nuclides, may cause gamma instrument software to report a false detect of a reactor product. In one case, a common reactor product (Cs-137) can interfere with and cause a false positive of a less-common reactor product (I-129). The magnitude of a gamma spectroscopy false positive depends on the interferor concentration in the sample, and the ratio of the target/interferor peak abundance.

Table 1. Peak interferences in environmental gamma spectroscopy samples

FALSELY DETECTED NUCLIDE	GAMMA PEAK (keV)	INTERFEROR NUCLIDE	INTERFEROR'S GAMMA ENERGY (keV)	INTERFEROR'S PEAK ABUNDANCE (%)
Eu-155	86.5	Pb-212, Pb-214	87.2	8
Eu-155	105.3	Ac-228	105.0	1.6
Mn-54	834.8	Ac-228	835.6	1.8
Zr-95	724.2	Tl-208	722.3	0.2
Zr-95	756.7	Ac-228	755.2	1.1
Cs-134	795.8	Ac-228	794.7	4.6
Pm-146	453.9	Bi-212	452.8	0.3
Np-239	99.5	Ac-228	99.5	1.3
Np-239	106.1	Ac-228	105.0	1.6
Np-239	117.0	Pb-212	115.2	0.6
Np-239	228.2	Pa-234	227.2	5.6
Np-239	277.6	Tl-208	277.4	6.5
I-129	29.6	Cs-137	32.1	3.8

In most examples above, the energy difference between the natural nuclide’s peak and the target nuclide’s peak exceeds the instrument resolution of 0.5 keV. Therefore, incorrect reported detects of Eu-155, Mn-54, Zr-95, Cs-134, Pm-146, and Np-239 can be recognized and suppressed during manual data review, if personnel are aware of the interferences.

FALSE POSITIVES IN LIQUID SCINTILLATION COUNTING

Liquid Scintillation Counting (LSC) is used for beta emitters which do not emit gamma rays, in situations where very low detection limits are not required. Nuclides quantitated by LSC include H-3, C-14, Ni-63, Tc-99, Pm-147, Sm-151, and Pu-241. LSC energy peaks are very wide: the Tc-99 beta peak approaches 300 keV in width (compared with 1-2 keV for gamma peaks). The extreme width of beta peaks means that if two beta-emitting nuclides are present in a sample, their peaks will probably overlap, making quantitation or even identification difficult to impossible. For this reason, most LSC analytical methods involve chemical separation, followed by analysis of the final solution.

The success of an LSC determination depends on complete chemical separation of the target nuclide from all other beta emitters. Chemical yield of the separation is determined by use of a carrier (e.g. stable CaCO_3 for C-14) or a tracer (e.g. Tc-99m for Tc-99). Furthermore, each sample batch contains a sample spiked with a known amount of the target nuclide. These QA/QC practices ensure that instrument efficiency and precision, and chemical recovery are known and kept within acceptable limits. However, no commercial laboratory providing services to SRS routinely tests whether chemical separation is complete (e.g. determines whether Pm-147 was completely separated from Sm-151, Eu-155, or beta-emitting actinides).

An example of a Pm-147 false positive due to incomplete chemical separation is shown in Figure 1. On the left is an LSC spectrum for a Pm-147 calibration standard; it represents what a Pm-147 peak is supposed to look like. The “crest” of the peak resides around Channel 500, and there is a sharp right-hand edge at Channel 680, which represents the beta endpoint energy. On the right is a spectrum from a quench-matched SRS soil sample. Instead of one peak present, there are two. It is clear that the chemical separation process failed for this sample. Furthermore, neither of the two peaks present have a “crest” at channel 500, and neither have a sharp right-hand edge at Channel 680. There are two nuclides in this samples, and neither one is Pm-147!

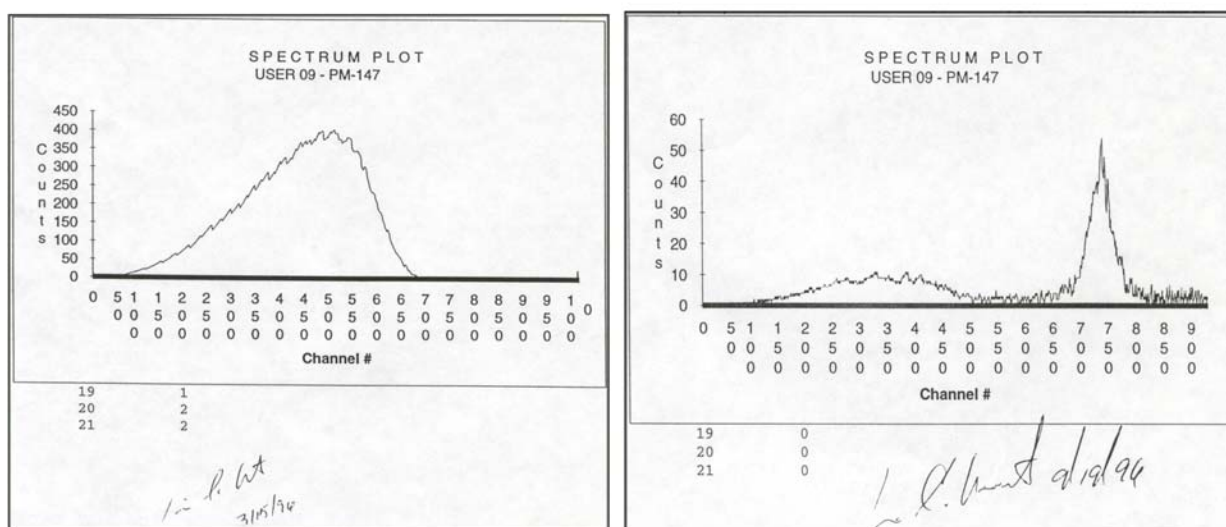


Figure 1. False positive of Pm-147 in soil. Reference standard (left); soil sample (right).

In order to guard against technical failures of this type, this particular laboratory’s QA/QC program requires that each spectrum be manually inspected by three people. This was done per procedure for the sample on the right. Three signatures are present (only one is visible in the cropped figure provided). However, the reviewers evidently did not carefully examine the spectrum before approving it. Virtually every reported Pm-147 detect in environmental samples reported to SRS, through 2003, has shown this same chemical separation failure, and is a false positive. Admittedly, chemical separation of trivalent Pm from all other lanthanides, trivalent actinides, and yttrium may be difficult. Manual review of spectra can identify when separation has succeeded, and when it has not. However, the example above shows that this manual review is not always performed correctly at the lab.

Pm-147 is not the only LSC analyte subject to false positives due to incomplete chemical separation. In SRS environmental samples, groundwater analyses of C-14, Ni-63, and Tc-99 have been reported as false detects, due to interference from tritium, which is common in many SRS groundwater samples.

Laboratories may reduce their false positive rate not only by more careful manual data review, but also by prudent selection of counting windows. In the Pm-147 sample spectrum shown above, the counting window was chosen to be the entire spectrum; all instrument counts between channels 1 and 914 contributed to the sample result. The laboratory could have chosen a counting window between channels 1 and 650; this would have eliminated false counts from one of the two nuclides which broke through into the final separate. False positives of Pm-147 would

not be completely eliminated by tightening the window; one of the interfering nuclides would have still been misidentified as Pm-147. However, the magnitude of the false positives, and possibly their frequency, would have been reduced with a better-chosen window.

For guarding against interference by tritium, counting windows can easily be chosen so as to completely exclude tritium counts. If the low-energy edge of the window is set above tritium's beta-energy endpoint of 19 keV, then tritium betas will not be counted as the target nuclide.

FALSE POSITIVES IN ALPHA SPECTROSCOPY

Alpha spectroscopy is the method of choice for most alpha-emitting actinides, including isotopes of Th, U, Np, Pu, Am, and Cm. Detection limits are very low, because background alpha particles can be easily stopped by shielding. Chemical separation of target nuclides from the rest of the sample is necessary, for two reasons. First, to remove extraneous mass in order to minimize self-absorption of alpha particles. Second, to remove interfering alpha emitters with the same energy as the target nuclide.

Environmental sample analyses by alpha spectroscopy are susceptible to false positives by two causes: (1) peak interference due to incomplete chemical separation, and (2) peak interference due to "taildown" or extension of one nuclide's peak into another nuclide's Region Of Interest (ROI).

Alpha Spectroscopy: Incomplete Chemical Separation

The problem of interfering nuclides due to incomplete chemical separation is acute in alpha spectroscopy, because multiple interferences are possible. For example, Th-228, Am-241, Rn-222, and Pu-238 – two naturally occurring nuclides, and two reactor products – all have essentially the same alpha particle energy. Because detection limits are low, only a slight amount of chemical breakthrough during sample preparation can generate a false detect.

Although each alpha spectroscopy analytical method has an associated chemical separation designed to defeat interferences, we have found that in commercial labs used by SRS, chemical separation often fails for selected analytes, resulting in the possibility of non-target analyte counts being misidentified.

An example is shown in the Am/Cm spectra shown in Figure 2. On the left is a reference standard containing Am-243, Am-241, and Cm-244. The long U-shaped markings delineate the ROIs, within which counts are attributed to the target nuclide. The Cm-244 ROI was selected to tightly encompass the Cm-244 reference standard. On the right is an SRS soil sample run by a commercial lab, reported as a detect for Cm-244. However, the counts within the

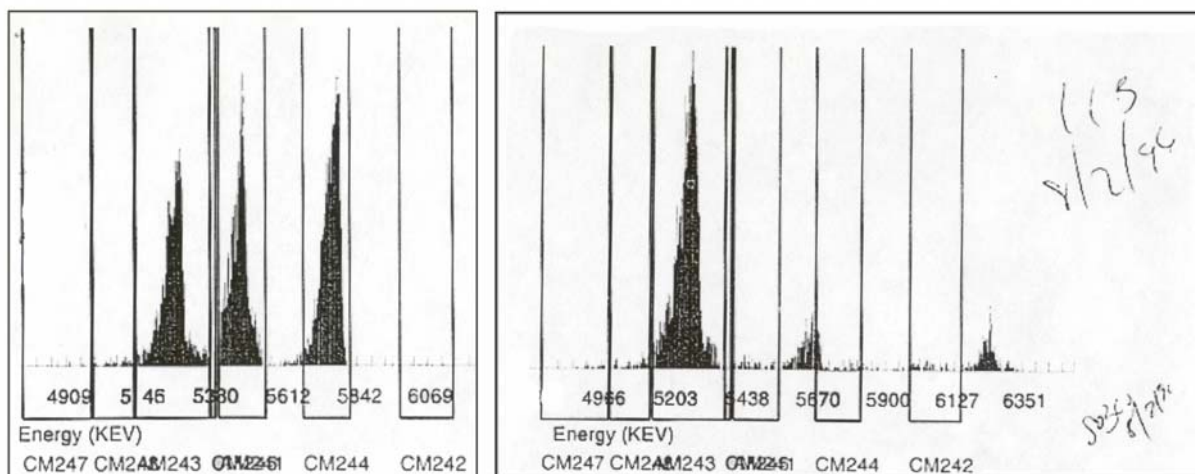


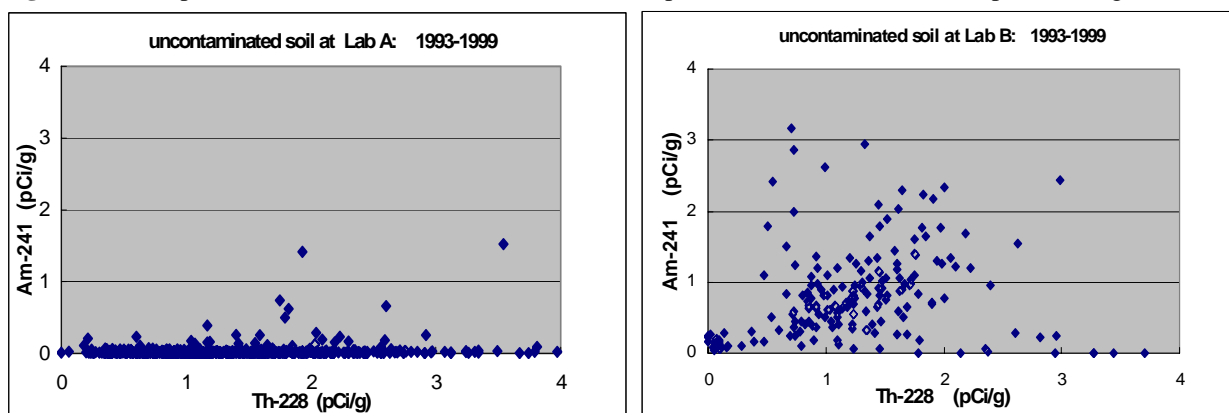
Figure 2. False positive of Cm-244. Reference standard (left); soil sample (right).

Cm-244 ROI are not from Cm-244, but rather arise from naturally-occurring Ra-224, whose alpha peak mostly misses the Cm-244 ROI, but slightly overlaps it. In addition to the Ra-224 peak, a second peak of a non-target nuclide is seen to the right of the Cm-242 ROI. This peak is attributable to Rn-220, the daughter of Ra-224. Like the Pm-147 spectrum shown above, this Am/Cm spectrum was approved and signed by three reviewers (only two signatures are visible in the cropped figure). The false Cm-244 detect could have easily been recognized, but evidently was not.

False detects of Cm-244 due to Ra-224 are easy to spot, but some false positives due to incomplete separation are more difficult, because their alpha particle energies are close. An example is Th-228 interference with Am-241 analysis. The peaks of these nuclides are more than 100 keV wide, but their centroids are only 60 keV apart.

During the 1990s two commercial labs provided Am-241 analyses of soil to SRS. Lab B consistently reported higher Am-241 results than Lab A (see Figure 3). The figure compares Am-241 to Th-228 in soil samples interpreted as probably uncontaminated with TRU (Pu-239 not detected).

Figure 3. False positives of Am-241. Successful chemical separation (left); unsuccessful separation (right).



Lab B reported detections of Am-241 at a much greater rate than Lab A. These detects were not randomly produced: Am-241 was detected only in samples where Th-228 was also detected. Spectra from Lab B showed that many samples with reported Am-241 had recognizable peaks in the 4000 keV region, which can be produced only by Th-232. The conclusion was that chemical breakthrough of natural Thorium (Th-228 & Th-232) occurred in Am-241 samples, producing high bias or false positives of Am-241. Lab B was requested to prepare a Thorium blank spike and analyze it for Am-241; this was done and nearly 100% breakthrough of Th-228 was demonstrated. Lab B conducted an internal investigation; it was found that laboratory personnel did not follow the lab's Standard Operating Procedure correctly; one important wet chemistry step was always omitted.

In addition to Cm-244 and Am-241, false positives due to incomplete chemical separation have also been observed in Np-237, Pu-238, and Am-243 analyses.

Alpha Spectroscopy: Taildown

Alpha particles lose energy when they encounter other atoms; therefore many alpha peaks show a "tail" on the low energy side (see Cm-244 tracer peak, above on left). If detector vacuum has degraded, or if sample mass on the planchet is too high, or if tracer spike amount is too high, then taildown may extend into the ROIs of neighboring nuclides. This is commonly observed at SRS contract labs in Thorium samples. The Th-229 tracer peak will often show taildown into the adjacent Th-230 ROI, causing Th-230 false positives in both samples and method blanks. Taildown is almost impossible to avoid in SRS Cm-245/6 samples, due to the neighboring Am-241 peak. Taildown has also been observed to affect U-235 analyses on occasion.

A summary of alpha spectroscopy false positives observed at commercial laboratories over the period 1993-2003 is given in Table 2.

Table 2. Summary of false positives in alpha spectroscopy.

AFFECTED NUCLIDE	CAUSE OF INTERFERENCE	RESPONSIBLE NUCLIDE	FREQUENCY OF OCCURRENCE*
Th-230	taildown	Th-229 tracer	high
U-235	taildown	U-234	low
Np-237	incomplete separation	U-234	low
Pu-238	incomplete separation	Th-228	moderate
Am-241	incomplete separation	Th-228	high
Am-243	incomplete separation	Th-228	(few samples examined)
Cm-243/244	incomplete separation	Ra-224	moderate
Cm-245/246	taildown	Am-241	high

*before corrective action or termination of laboratory services

EFFECTS OF FALSE POSITIVES ON ENVIRONMENTAL CHARACTERIZATION

The presence of radiological false positives in environmental or waste characterization may impact data users in three ways:

- False positives **above** an action level, in a radiologically **clean** unit, cause unnecessary characterization / remediation. Or, hazardous waste may be misidentified as mixed waste.
- False positives **below** an action level, in a radiologically **clean** unit, may trigger questions from regulators and/or the public. Characterization may be longer and more expensive than necessary.
- False positives **above** an action level, in a radiologically **contaminated** unit, may cause risk and/or exposure pathways to be overstated. Characterization may be longer and more expensive than necessary.

A table showing false positive rates, magnitudes, and comparison with an EPA action level is shown below. Data represent SRS soil samples collected between January 1995 and July 2003. For Am-241, 249 samples are represented. For other nuclides, the sample set ranges from 1180 to 5950 samples. Identification of false positives were made by comparing observed vs. expected peak shapes and energies on instrument printouts.

Table 3. False positive frequency and magnitude in SRS soils.

nuclide	Raw % detection rate (1995-2003)	% False Positive (FP) rate ('95-'03)	median FP (pCi/g)	highest FP in a clean sample (pCi/g)*	highest FP (pCi/g)	Risk Based action level (pCi/g)#
Mn54	42	>40	0.02	0.3	7	0.7
Zr95	31	31	0.03	0.4	8	3.9
I129	28	27	0.7	NA**	399	2.5
Cs134	1	0.5	0.1	0.2	0.2	0.16
Pm146	7	6	0.01	0.2	4	0.13
Eu155	49	>40	0.1	1.7	80	3.8
Am241***	53	44	0.9	5.4	6.6	2.0
Cm243/244	21	4	0.05	5.5	5.5	0.35
Cm245/246	13	>4	0.05	NA**	1.4	0.4

*a soil sample with Cs-137 <0.2 pCi/g and Pu-239 not detected

EPA Region 9 Preliminary Remediation Goal

**interfering nuclide is manmade, so false positives will not occur in clean sites

***Lab B results only; 1993-1999. Lab A results were satisfactory.

Four nuclides, Cs-134, Pm-146, Am-241, and Cm-243/244, each showed at least one false positive above the EPA Action Level in a clean soil sample.

A similar table for groundwater is shown in Table 4:

Table 4. False Positive frequency and magnitude in SRS groundwater.

nuclide	% detection rate (1995-2003)	% False Positive (FP) rate ('95-'03)	median FP (pCi/L)	highest FP (pCi/L)	Risk Based action level (pCi/L)*
Ba133	0.4	0.2	8	16	7
Cs134	0.3	0.3	5	23	1.1
Pm146	0.5	0.4	9	16	11.4
Eu152	0.3	0.3	13	37	7.8
Eu154	0.5	0.5	16	58	4.6
Eu155	0.5	0.4	20	69	25
Th230	25	9	0.4	19	0.52
C-14	32	1.3	900	250000	1.3

*EPA Region 9 Preliminary Remediation Goal

Groundwater is a cleaner matrix than soil, with few indigenous peak interferences. In the examples shown, only C-14 shows false positives due to an interfering nuclide actually present in the aquifer: tritium. Therefore, the C-14 false positives, though high, only occur in water which is already significantly contaminated. False positives of the other nuclides are caused either by a peak interferor introduced at the lab (Th-230, from the Th-229 tracer), or by random fluctuations in instrument background (Ba-133, Cs-134, Pm-146, Eu-152, Eu-154, Eu-155). These false positives are recognized during data review by the peak width ("Full Width at Half Max", FWHM) being too broad. Although their occurrence rate is low (<0.5%), they add up: a 20-nuclide gamma scan performed on 20 groundwater samples will generate 400 analytical records; 2 of these may be expected to be false detects, suppressible by manual review of raw data. All nuclides shown in this table have *median* false positive magnitudes which exceed or approach the EPA Region 9 Preliminary Remediation Goals.

WHAT SHOULD DATA USERS DO?

1. **Trust your instinct.** If you receive detected results of a nuclide which should not be present based on historical knowledge, check it out.
2. **Do not send alpha spectroscopy and LSC samples to labs which cannot save copies of sample spectra.** Such labs are 10 years behind the pack; if laboratory personnel cannot produce spectra, you and they both will be unable to recognize peak interferences when they occur.
3. **Be aware of possible interferences in your samples.** Examples given in this paper are from the Savannah River Site, where time-since-last-fission is 20 to 40 years in most waste units, and where soils contain about 1 pCi/g of natural U-238, Th-232, and their progeny. Samples from operating or recently closed reactors may be subject to other peak interferences not discussed here. Also, the magnitude of peak interferences due to naturally occurring radionuclides will vary, depending on local NORM concentrations. Be ready to inspect raw data for peak overlaps, taildown, FWHM, etc.
4. **Discuss possible interferences with laboratory personnel.** Do **not** assume that analysts know about them: all radiological labs reviewed in this study unknowingly produced easily avoidable false positives due to peak interferences. Automatic interference correction routines may work well in highly radioactive samples, but at concentrations near environmental action levels, high relative uncertainties usually preclude their successful use.

5. **Discuss possible interferences with data validators.** Do **not** assume that validation personnel know about them: data validation guidance documents from EPA, DOE, and other organizations do not always treat peak interferences adequately.
6. **If you suspect incomplete chemical separation at the lab, but spectra are inconclusive or unavailable, do an interference study.** If A may interfere with B, and you have unexpected detects of B, have the lab prepare spiked blanks of A, and analyze them for B. A detection of B indicates a failed chemical separation.
7. **Resist the urge to get “additional nuclides at no added cost” in gamma and alpha spectroscopy.** Request only nuclides you actually need. The more data you get, the more false positives you get.