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Decision Support Council Chemistry Team:

Recommendation for Qualification of the ER Project Gamma Spectroscopy Data Set

1.0 PURPOSE

The Decision Support Council Chemistry Team is recommending that administrative qualifiers and corresponding reason codes be applied to most of the radionuclides included in the ER Project gamma spectroscopy suite. The ER Project gamma spectroscopy suite is a requirement of the 1995 statement of work for analytical services (LANL 1995, 49738), and has been in use by the subcontract analytical laboratories since April, 1995. Table 1 presents the recommended qualifiers and reason codes for the gamma spectroscopy suite. The administratively-applied qualifiers and reason codes are intended to inform data-users about several attributes of the ER Project gamma spectroscopy data set that may affect data use. The qualifiers and reason codes will be placed in the appropriate FIMAD database table. For 36 of the 43 gamma spectroscopy analytes, professional judgment should be exercised in the use of gamma spectroscopy data. This document provides the recommendations and the rationale for data qualification. This document should be read by ER Project chemists, statisticians, and risk assessors, and any other users of the ER Project gamma spectroscopy data set.

2.0 INTRODUCTION

In April 1995, the ER Project adopted a protocol for an electronic data deliverable (EDD) that is based on a spreadsheet format with fixed field definitions. Because field definitions are fixed (that is, the laboratories cannot define new fields), it was necessary to define a fixed analyte suite for the gamma spectroscopy analysis performed under the 1995 ER Project statement of work for analytical services. Adoption of a standardized suite also ensured that a consistent set of target analytes would be measured and reported by all subcontractor laboratories performing analyses of ER Project samples.

Analytical data received in the EDD format is uploaded to the FIMAD stage tables. The stage table data set has undergone extensive editing and cleanup in 1997, and will be moved to the production tables (ANYL_MASTER and ancillary tables) in the fall of 1997. Prior to moving the data set, the Chemistry Team is recommending that qualifiers be placed on the results for most of the gamma spectroscopy analytes. (Seven analytes require no qualification.) This document presents the recommendations for these administratively-applied qualifiers. The qualifiers and reason codes are intended to inform data users of certain attributes that will affect data use, and to alert data users to potential limitations in the quality of the data. Therefore, this document should be read by ER Project chemists, statisticians, and risk assessors, and any other users of the ER Project gamma spectroscopy data set.

The gamma spectroscopy qualifiers and associated reason codes will be placed in the FIMAD_LANL_Qualifiers table by the FIMAD database administrator.

2.1 The current ER Project gamma spectroscopy suite

The current ER Project gamma spectroscopy analyte suite that is defined in the analytical services statement of work consists of the 43 radionuclides listed in Table 2. The radionuclides included in the suite were drawn from the following four sources.

1. Radionuclides present on the 1995 ER Project screening action levels (SALs) list that can be measured by gamma spectroscopy, mostly fission and activation products. Also included are selected progeny of these radionuclides that can be measured by gamma spectroscopy.

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2. Any radionuclide that had previously been requested by the ER Project, or that has been consistently reported by the subcontractor laboratories.

3. Naturally occurring gamma-emitting radionuclides in the actinium, thorium, and uranium decay series amenable to gamma spectroscopy measurement, as well as K-40 and annihilation radiation. These naturally occurring radionuclides, *with the exception of U-235*, are included primarily as "data quality" analytes to provide an indication of the quality of the gamma spectroscopy measurement. They are not intended to be evaluated as potential primary radiological contaminants at ER Project sites.

4. "Quality control" radionuclides typically used by the analytical laboratory in their laboratory control samples for instrument calibration and checks on instrument performance. The recovery of these analytes from quality control samples is used by the ER Project baseline validation procedure and the ER Project chemists to evaluate the quality of the measurement. These radionuclides are not typically expected to be present in ER Project samples because of their short half-lives, and should have no direct use in risk assessment.

2.2 Proposed qualifiers and reason codes

The proposed qualifiers and corresponding reason codes are described in Table 1. Five new reason codes, R16a through R16e, and corresponding qualifiers are proposed for the gamma spectroscopy data set. These qualifiers and reason codes will be applied to the electronic data by the FIMAD database administrator.

As seen in Table 2, the gamma spectroscopy suite can be broadly divided into three categories: (1) fission and activation products; (2) naturally occurring decay series "data quality" radionuclides *(excluding U-235)*; and (3) "quality control" radionuclides. The Chemistry Team recommendation for data qualification is based on the following considerations.

- Fission and activation products with half-lives less than 365 days are typically not evaluated as historic contaminants at ER Project sites. Generally, historical releases of radionuclides with half-lives less than one year will have decayed to insignificant quantities if the site has been inactive (or if radionuclides have not been used at the site) for at least 10 half-lives of any suspected radionuclide contaminant.
- There are a number of redundant measurements of naturally occurring decay series progeny, where measurement of only two or three progeny in each decay series would provide adequate information. Some of the progeny are not as reliably measured by gamma spectroscopy as others in the same decay series.
- It has become apparent in two years of usage that gamma spectroscopy is not a reliable measurement technique for certain radionuclides. The naturally occurring radionuclides have varying detection limits so that there is difficulty in deciding whether elevated levels are present. The quality of the gamma spectroscopy measurement for other radionuclides does not meet the requirements of the ER Project due to interference in the gamma spectrum. Data for these radionuclides should be used only after review by a technical expert.
- "Quality control" radionuclides are included to provide information about the quality of the gamma spectroscopy measurement and are not intended for evaluation as potential historical contaminants at ER Project sites.

3.0 RECOMMENDED QUALIFICATIONS

3.1 No administrative qualification

Gamma spectroscopy analytes that require no administrative qualification include U-235 and seven fission and activation products. Uranium-235 is naturally-occurring in LANL soils and tuff, and may also be present due to historical operations. These radionuclides are typically evaluated as potential historical contaminants at ER Project sites.

The gamma spectroscopy analytes that require no qualification include fission and activation products that meet the following three criteria: (1) half-life of greater than 365 days; (2) non-gaseous; and (3) good gamma emission and detection properties. Good gamma emission properties include sufficiently high gamma intensity (ratio of emissions per disintegration); peaks within the instrument's sensitive range; single or easily deconvoluted peaks; high peak to baseline ratio; and peaks falling on the flatter portion of the baseline (not on a Compton edge). The seven radionuclides that meet these criteria are: Am-241, Co-60, Cs-134, Cs-137, Eu-152, Na-22, and Ru-106. It should be noted that qualifiers may be applied to data for these radionuclides as part of the ER Project baseline validation procedure.

3.2 Reason Code R16a

Reason code R16a is applied to fission and activation products measured by gamma spectroscopy with half-lives less than 365 days. These anthropogenic radionuclides may be associated with historical releases, depending on the age of the release. A "P" qualifier flag is applied to indicate that professional judgment should be exercised in the use of data for these radionuclides, taking into consideration past and current activities at the site. The following six radionuclides are qualified with reason code R16a: Ce-144, Co-57, Mn-54, Pa-233, Se-75, and Zn-65.

3.3 Reason Code R16b

Reason code R16b is applied to radionuclides that are not reliably measured by gamma spectroscopy. A "PM" qualifier flag is applied to indicate data quality limitations exist due to poor sensitivity or interference in the gamma spectrum that lead to large uncertainties in identification and quantitation. A manual check of the hardcopy data package is recommended. Professional judgment should be exercised in the use of gamma spectroscopy data for the following radionuclides: Ac-228, Ba-140, Bi-212, I-129, La-140, Np-237, Pa-231, Pa-234m, Pb-210, Pb-211, Ra-223, Ra-224, Ra-226, and Rn-219. If any of these radionuclides are suspected contaminants at an ER Project site, the Chemistry Team can be consulted about alternative measurement methods.

There are particular data use concerns for four naturally occurring radionuclides: Pa-231, Pa-234m, Pb-210, and Ra-226. The radionuclides Pa-231 and Pa-234m occur early in the U-235 and U-238 decay series, respectively. As discussed further in Section 3.4, these radionuclides may provide an indication of the presence of U-235 or U-238 for which there has not been sufficient time for ingrowth of the later progeny to measurable concentrations. However, both Pa-231 or Pa-234m have poor characteristics for reliable quantitation by gamma spectroscopy. Interpretation of the results for these radionuclides requires some technical expertise, and the data should be reviewed by a technical expert prior to use. For this reason, it is not recommended that these radionuclides be used as primary indicators for uranium contamination, but they may provide corroboration of isotopic uranium results.

The radionuclides Pb-210 and Ra-226 may be considered to be primary radionuclides for risk assessment purposes. Gamma spectroscopy is not the preferred analytical method for these radionuclides. The gamma spectrum of Ra-226 is subject to interference from U-235, and an adequate in-growth period to reach equilibrium with the radon progeny must be allowed in order to obtain a reliable measurement. Preferred analytical methods for Ra-226 are chemical separation and alpha emission measurement (soil samples); or radon emanation (water samples). The

gamma spectrum of Pb-210 is subject to interference from low energy x-rays. Preferred analytical methods for Pb-210 include chemical separation and beta emission analysis by liquid scintillation counting or gas-flow proportional counting.

3.4 Reason Code R16c

Reason code R16c is applied to certain naturally occurring radionuclides that are reliably measured by gamma spectroscopy, and that can provide an indication of the quality of the gamma spectroscopy measurement. Selected naturally occurring progeny in the actinium, thorium, and uranium decay chains, as well as annihilation radiation and K-40, are included in the gamma suite as "data quality" analytes. Measurement of more than two or three progeny in a decay series is redundant; therefore, only the radionuclides with good gamma spectroscopy features are qualified with reason code R16c. The qualifier flag "P" is applied to indicate that professional judgment should be exercised in the use of data for the following analytes: Bi-211, Bi-214, K-40, Pb-212, Pb-214, Th-227, Th-234, Tl-208, and annihilation radiation.

The "data quality" analytes are not typically evaluated as potential contaminants because historical operations at the Laboratory employed materials that had been processed off-site to remove these progeny. Therefore, *with the few exceptions discussed below*, historical operations at LANL are unlikely to have enhanced the levels of these naturally occurring radionuclides in environmental media. For example, for a hypothetical release of processed uranium that occurred 50 years ago, the activity ratio for most of the progeny is insignificant and they would not be detected by routine gamma spectroscopy measurements. Further description of the decay series equilibrium relationships can be found in *EPA Guidance for Data Useability in Risk Assessment (Part B)* (EPA 1992, 56474).

The "data quality" radionuclides are primarily intended to provide an indication of the quality of the gamma spectroscopy measurement. Measurements of naturally occurring radionuclides known to be present in Laboratory soils can serve two purposes.

1. Provide an indication of the quality of the gamma spectroscopy measurement. Background values are available for the parent radionuclides and some of their progeny, and can be used to evaluate whether the measured values are reasonable. Failure to detect some or all of the naturally occurring radionuclides may indicate decreased sensitivity in the measurement that would impact the ability to detect potential contaminant radionuclides.
2. Provide an indication of locally elevated background concentrations of uranium and thorium isotopes. Data for certain of the progeny radionuclides can be useful when evaluating values reported for Th-232, U-235, or U-238 (usually measured by alpha spectrometry) because the relative activity concentration of parent and progeny isotopes is a known quantity.

The results for the most of the naturally occurring radionuclides included in the gamma spectroscopy suite are not typically included in a risk-based screening assessment. If a uranium or thorium release is suspected at a site, the progeny radionuclides are not evaluated separately because their emissions are typically included in the dose conversion factors for the appropriate parent radionuclides.

There are three naturally occurring radionuclides measured by gamma spectroscopy that are early progeny in the decay series. Pa-231 is the decay product of U-235 (via Th-231), and may be an indicator for the presence of U-235 for which there has not been sufficient time for ingrowth of the later progeny to measurable concentrations. Similarly, Th-234 and Pa-234m may be indicators for the presence of U-238. The amount of elevation above background for these progeny will depend on the age of release. (LANL-specific background values are not available for these radionuclides.) Unfortunately, the radionuclides Pa-231 and Pa-234m are not reliably measured by gamma spectroscopy and therefore are qualified with reason code R16b (see

Section 3.3). Of the three radionuclides, only Th-234 is reliably measured by gamma spectroscopy and may provide an indication of the presence of uranium contamination or corroboration of isotopic uranium results. However, if uranium contamination is suspected at a site, analysis for uranium isotopes using alpha spectrometry or mass spectrometry is strongly recommended.

Potassium-40 is a primordial radionuclide that occurs in combination with all forms of stable potassium. It is present in LANL soil and tuff samples at levels ranging from approximately 15 to 40 pCi/g. (A reliable LANL-specific background value for K-40 is not available.) Potassium-40 is easily and reliably measured by gamma spectroscopy, and is a prominent feature in the gamma spectra of LANL soils. Therefore, this radionuclide provides an excellent indication of the quality of the gamma spectroscopy measurement. Because K-40 should be readily detected in LANL soil samples, the K-40 results for laboratory duplicate samples can be used to estimate the precision of the gamma spectroscopic measurement. Potassium-40 may also be formed as an activation product, but anthropogenic sources of K-40 due to historical operations are not known to exist at any ER Project sites.

Annihilation radiation is a pervasive gamma emission at 511 keV that has several sources. It can be useful to confirm the presence of a positron emitter, such as Na-22, or large activities of very energetic gamma emitters, such as Co-60. However, its main application is as a data quality indicator. Given its pervasive nature, it is expected to be detected in almost every analysis where sufficient count time and sample size are being used. Failure to detect the annihilation radiation may indicate that the energy calibration of the system has shifted.

3.5 Reason Code R16d

The reason code R16d is applied to six radionuclides typically used by the analytical laboratory in their laboratory control samples for instrument calibration and checks on instrument performance. The "quality control" radionuclides typically used in laboratory control samples are Cd-109, Ce-139, Hg-203, Sn-113, Sr-85, and Y-88. As part of the ER Project baseline validation process, the results for some or all of these radionuclides in quality control samples are used to determine the control status of the measurement. They are not typically expected to be present in ER Project samples because of their short half-lives. The qualifier flag "P" is applied to indicate that professional judgment should be exercised in the use of data for these radionuclides.

4.0 REFERENCES

LANL (Los Alamos National Laboratory), July 1995. "Statement of Work - Analytical Support," Revision 2, RFP No. 9-XS1-Q4257, Los Alamos, New Mexico. **(LANL 1995, ER ID Number 49738)**

EPA (US Environmental Protection Agency), May 1992. "Guidance for Data Useability in Risk Assessment (Part B), " Publication 9285.7-09B, Office of Emergency and Remedial Response, Washington, DC. **(EPA 1992, ER ID Number 56474)**

Table 1

Recommended Qualifications for the ER Project Gamma Spectroscopy Suite

LANL Qualifier	LANL Reason Code	Analytes Qualified	
None	None	Am-241 Co-60 Cs-134 Cs-137	Eu-152 Na-22 Ru-106 U-235
P: Data use should be based on professional judgment.	**R16a**: Anthropogenic radionuclide measured by gamma spectroscopy with half-life less than 365 days.	Ce-144 Co-57 Mn-54 Pa-233 Se-75 Zn-65	
PM: Data use should be based on professional judgment. Manual review of the raw data is recommended.	**R16b**: Radionuclide is not reliably measured by gamma spectroscopy.	Ac-228 Ba-140 Bi-212 I-129 La-140 Np-237 Pa-231	Pa-234m Pb-210 Pb-211 Ra-223 Ra-224 Ra-226 Rn-219
P: Data use should be based on professional judgment.	**R16c**: Naturally occurring radionuclide measured by gamma spectroscopy.	Bi-211 Bi-214 K-40 Pb-212 Pb-214	Th-227 Th-234 Tl-208 Annihilation radiation
P: Data use should be based on professional judgment.	**R16d**: Radionuclide measured by gamma spectroscopy for quality control purposes only.	Cd-109 Ce-139 Hg-203 Sn-113 Sr-85 Y-88	

Table 2

ER Project Gamma Spectroscopy Suite (April 1995 to present)

Analyte	Half-Life	LANL Qualifier / Reason Code	Comment
Activation products (and their decay products)			
+ Am-241	432.2 y	None	Potential historical contaminant.
0 Co-67	270.9 d	P / R16a	Half-life less than 365 d.
+ Co-60	5.271 y	None	Potential historical contaminant.
0 Mn-54	312.5 d	P / R16a	Half-life less than 365 d.
+ Na-22	2.602 y	None	Potential historical contaminant.
0 Np-237	2.14×10^6 y	PM / R16b	Not reliably measured.
Pa-233	27.0 d	P / R16a	Half-life less than 365 d.
0 Se-75	119.78 d	P / R16a	Half-life less than 365 d.
Zn-65	243.9 d	P / R16a	Half-life less than 365 d.
Fission products			
Ba-140	12.74 d	PM / R16b	Not reliably measured. Half-life less than 365 d.
0 Ce-144	284.3 d	P / R16a	Half-life less than 365 d.
+ Cs-134	2.062 y	None	Potential historical contaminant.
+ Cs-137	30.0 y	None	Potential historical contaminant.
+ Eu-152	13.33 y	None	Potential historical contaminant.
I-129	1.57×10^7 y	PM / R16b	Not reliably measured.
La-140	40.272 h	PM / R16b	Not reliably measured. Half-life less than 365 d.
+ Ru-106	368.2 d	None	Potential historical contaminant.
Actinium series (progeny of U-235)			
Bi-211	2.14 m	P / R16c	Data quality analyte.
Pb-211	36.1 m	PM / R16b	Not reliably measured. Redundant with other progeny in decay series.
0 Pa-231	3.28×10^4 y	PM / R16b	Not reliably measured.
Ra-223	11.434 d	PM / R16b	Not reliably measured. Redundant with other progeny in decay series.
Rn-219	3.96 s	PM / R16b	Not reliably measured. Redundant with other progeny in decay series.
Th-227	18.718 d	P / R16c	Data quality analyte.
+ U-235	7.04×10^8 y	None	Naturally occurring and/or potential historical contaminant.

Analyte	Half-Life	LANL Qualifier / Reason Code	Comment
Thorium series (progeny of Th-232)			
Ac-228	6.13 h	PM / R16b	Not reliably measured. Redundant with other progeny in decay series.
Bi-212	60.55 m	PM / R16b	Not reliably measured. Redundant with other progeny in decay series.
Pb-212	10.64 h	P / R16c	Data quality analyte.
Ra-224	3.66 d	PM / R16b	Not reliably measured. Redundant with other progeny in decay series.
Tl-208	3.07 m	P / R16c	Data quality analyte.
Uranium series (progeny of U-238)			
Bi-214	19.9 m	P / R16c	Data quality analyte.
Pb-210	22.3 y	PM / R16b	Not reliably measured.
Pb-214	26.8 m	P / R16c	Data quality analyte.
Pa-234m	1.17 m	PM / R16b	Not reliably measured.
Ra-226	1600 y	PM / R16b	Not reliably measured.
Th-234	24.10 d	P / R16c	Data quality analyte.
Miscellaneous			
Annihilation radiation		P / R16c	Data quality analyte.
K-40	1.28×10^9 y	P / R16c	Data quality analyte.
Cd-109	462.0 d	P / R16d	Quality control analyte.
Ce-139	137.6 d	P / R16d	Quality control analyte.
Hg-203	46.60 d	P / R16d	Quality control analyte.
Sn-113	115.1 d	P / R16d	Quality control analyte.
Sr-85	64.84 d	P / R16d	Quality control analyte.
Y-88	106.6 d	P / R16d	Quality control analyte.