Radioanalytical Detection Status in Environmental Samples

National Environmental Monitoring Conference

August 2-5, 2021
Bellevue, WA

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Outline

1. Introduction
2. Definitions
3. History and Logic
4. Statistics and Data
5. Path Forward

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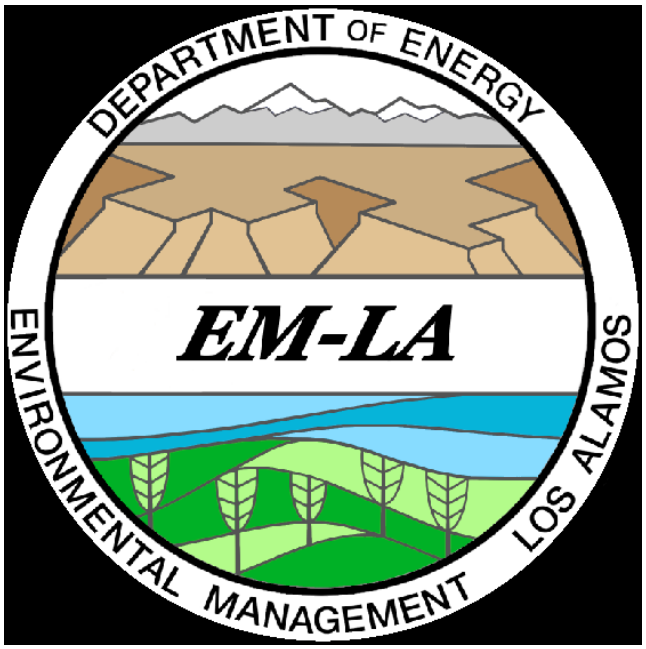
Introduction

- Newport News Nuclear BWXT-Los Alamos, LLC (N3B)
  - Owned by Newport News Nuclear, a division of Huntington Ingalls Industries, and BWX Technologies.
  - Manages the Los Alamos Legacy Cleanup Contract for the U.S. Department of Energy (DOE), Office of Environmental Management's Los Alamos Field Office.



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Introduction

- N3B's primary responsibility is to characterize, manage, and clean up legacy waste at Los Alamos National Laboratory (LANL).
  - Legacy waste:
    - Generated before 1999.
    - Includes radioactive material from the Manhattan Project and beyond.

- Some remediated areas will be turned over to Los Alamos County for industrial, commercial, or residential use

Introduction

- 2018 - New contract at LANL for the clean up of legacy waste
- Assessment of the process for data review leads to questions about detection status of low-level radionuclides
- Review of national and international standards reveals that the process was out of line with industry standards
- Reconfiguration of database automated data review module provides opportunities for improvement

Definitions

- **Decision Level (DL) or Critical Level (L_c)**
  - The minimum measured analyte quantity or concentration (*a posteriori* result) required to give a stated confidence (generally 95%) that a positive amount of the analyte is present.[1]
  - Expected to have a 5% chance for a false positive (probability of erroneously concluding a radionuclide is detected in a blank sample)[1]
    - Type α error
  - Similar to Method Detection Limit (MDL) used in standard chemistry

[1] ANSI/ANS-41.5-2012 (R2018), *American National Standard Verification and Validation of Radiological Data for Use in Waste Management and Environmental Remediation*

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Definitions

- **MDL**
  - The minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.[2]

[2] EPA 821-R16-006, *Definition and Procedure for the Determination of the Method Detection Limit,* Revision 2

Definitions

- **Minimum Detectable Concentration (MDC)**
  - The minimum quantity or concentration of a radionuclide required (*a priori*) to give a stated confidence (generally 95%) that the measurement result will be above the DL (detected).[1]
  - A sample spiked at the MDC is expected to have a 5% chance of a false negative (a sample spiked at the MDC will give a result below the critical level 5% of the time).
    - Type β error

[1] ANSI/ANS-41.5-2012 (R2018), *American National Standard Verification and Validation of Radiological Data for Use in Waste Management and Environmental Remediation*

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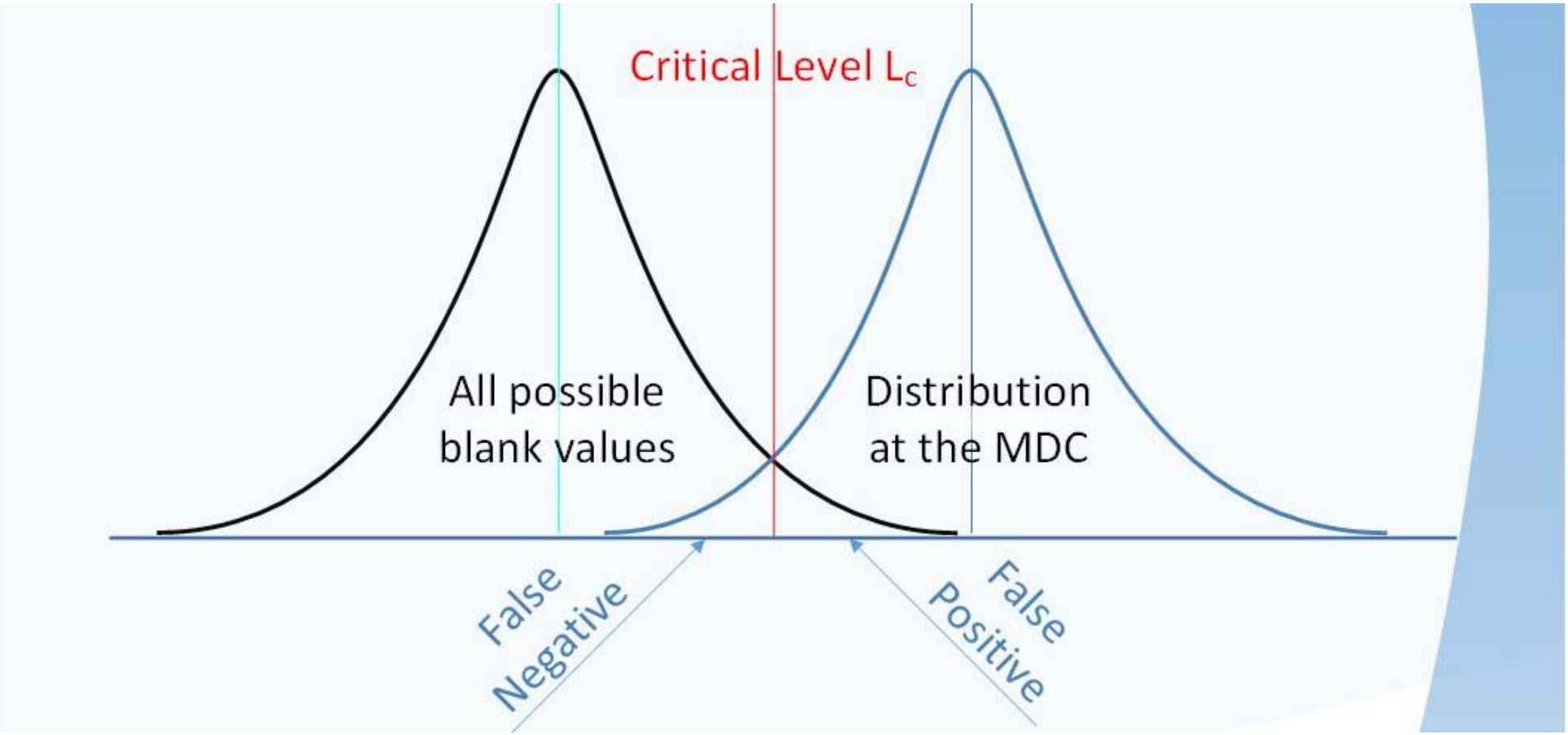
Definitions



What is a radionuclide detect?

- ANSI/ANS-41.5-2012: Verification And Validation Of Radiological Data For Use In Waste Management And Environmental Remediation
  - 4.7, Detectability - Each analyte's detection status shall be evaluated during the compliance verification and validation process. An analyte shall be considered as positively detected if the result is above the sample-specific Decision Level (DL) or Critical Level (Lc).

What is a radionuclide detect?

- NUREG-1576 EPA 402-B-04-001A NTIS PB2004-105421: Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP):
  - An analyte detection decision should be made by comparing the gross signal, net signal, or measured analyte concentration to its corresponding critical value.
  - A measurement result should never be compared to the minimum detectable value to make a detection decision.

Considerations

- How low do you need to go?
- What are the action levels?
- What are the consequences of a false positive?
- What are the consequences of a false negative?
- How much risk are you willing to accept?

These questions must be answered during development of project-specific data quality objectives.

DOE Benchmarking

- Various methods of determining a detected result are used across the DOE complex

> MDC

- Analyte is considered detected only if the result is >MDC
- Most commonly used

DOE Benchmarking

> MDC and > xσ TPU

- Analyte must be > than the MDC, and > than a specified σ total propagated uncertainty (TPU) level to be considered a detected result.
- If either criteria is not met, the result is considered not detected
- Fewest detects reported

DOE Benchmarking

> L_c

- Analyte is considered detected if the result is >L_c
- Complies with recommendations in most standards
- Set desired tolerance for false positive based on risk

Historical Detection Status Identification at LANL

Historical LANL Detection Criteria

- Result must be > MDC, and >3σ TPU
- Very few low-level detects reported

2014 Changes

- Dropped the 3σ TPU criteria
- Result must be > MDC
- Aligns with most DOE sites

2021 Changes

- Hybrid Approach
- Incorporate L_c
  - Comply with national and international standards and guidance documents
  - Maintain historical link

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Validation Qualifiers for Detection Status

U

- $< L_c$
- If the result is less than the L_c, the analyte is not detected

UJ

- $L_c <$ Result $<$ MDC
- The result is considered not detected, but is estimated
- Similar to general chemistry (estimated between MDL and PQL)
- Link to historical data through continuous use of U

NQ

- > MDC
- The result is considered to be detected

New Process

Laboratory reports results <MDC with "U" lab qualifier

Laboratory loads electronic data deliverable (EDD) in to N3B database hosted by Locus Technologies

Automated Data Review Module applies validation qualifiers to data based on new detection rules

After review, the data are released, and uploaded overnight to the public website

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Blank Data

Method Blanks associated with N3B data (2020-2021)

Blanks compared to MDC

Analyte	Detected	N	Percent > MDC
Gross Alpha	0	48	0.0%
Gross Beta	0	47	0.0%
U-234	4	263	1.5%
U-235	0	263	0.0%
U-238	3	263	1.1%
Natural Gamma	1	1854	0.1%
Am-241	0	111	0.0%
Pu-238	0	169	0.0%
Pu-239	2	169	1.2%
H-3	0	99	0.0%
Sr-90	1	72	1.4%
Non-Natural Gamma	0	1234	0.0%
Grand Total	**11**	**4592**	**0.2%**

Blanks compared to L_c

Analyte	> L_c	N	Percent > L_c
Gross Alpha	6	48	12.5%
Gross Beta	9	47	19.1%
U-234	28	263	10.6%
U-235	29	263	11.0%
U-238	21	263	8.0%
Natural Gamma	271	1854	14.6%
Am-241	26	111	23.4%
Pu-238	16	169	9.5%
Pu-239	11	169	6.5%
H-3	5	99	5.1%
Sr-90	12	72	16.7%
Non-Natural Gamma	60	1234	4.9%
Grand Total	**494**	**4592**	**10.8%**

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Data Discussion

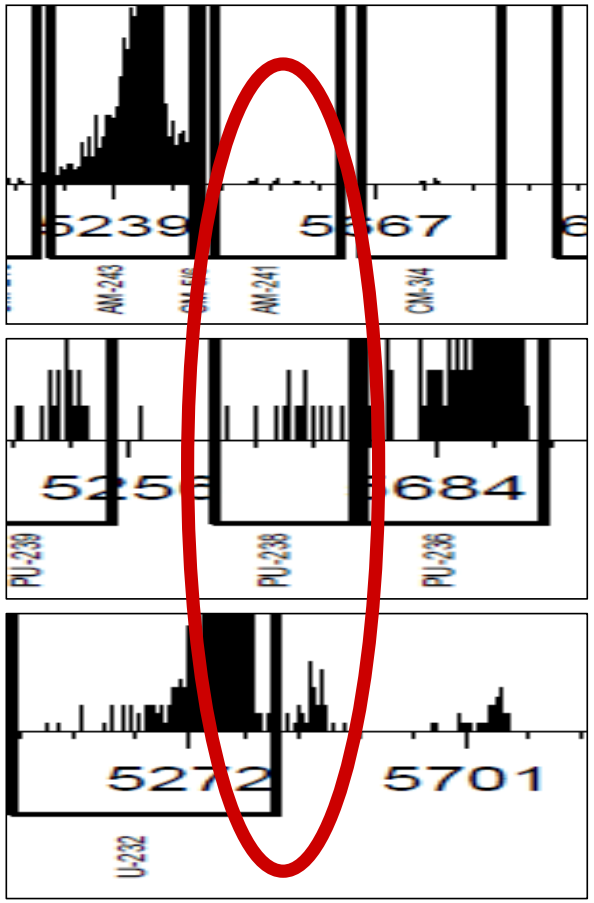
- Method blanks are assumed to be “true zero” samples
  - Assumes data reported was free of lab contamination or contribution from reagents, glassware, etc.
- Most non-natural radionuclides show near the expected 5% false positive
  - Exceptions:
    - Am-241
      - Spectral review indicates noise in this region of interest (ROI)
      - “Busy” ROI
    - Sr-90
      - Few data points
      - Nature of Gas Proportional Counting

Data Discussion

Americium Spectrum

Plutonium Spectrum

Uranium Spectrum



Data Discussion

- Natural radionuclides show higher propensity for false positives
  - Non-Poisson distribution
    - Natural radionuclides may be present in reagents, glassware, background environment, etc.
  - Per MARLAP, “If the analyte is a naturally occurring radionuclide that is present at varying levels in reagents, then a correction for the reagent contamination is necessary and expressions based on the Poisson model may be completely inappropriate.”
  - Is another calculation for L_c more appropriate for natural radionuclides?
    - Perhaps utilize blank population?

Blank Data

Method blanks associated with N3B data (2020-2021) compared to L_c

Liquid Matrix

Analyte	Detected	N	Percent > L_c
Gross Alpha	5	46	10.9%
Gross Beta	9	45	20.0%
U-234	2	65	3.1%
U-235	5	65	7.7%
U-238	3	65	4.6%
Natural Gamma	26	135	19.3%
Am-241	16	66	24.2%
Pu-238	6	64	9.4%
Pu-239	4	64	6.3%
H-3	3	13	23.1%
Sr-90	5	43	11.6%
Non-Natural Gamma	16	272	5.9%
Grand Total	**100**	**943**	**10.6%**

Solid Matrix

Analyte	Detected	N	Percent > L_c
Gross Alpha	1	2	50.0%
Gross Beta	0	2	0.0%
U-234	26	198	13.1%
U-235	24	198	12.1%
U-238	18	198	9.1%
Natural Gamma	245	1719	14.3%
Am-241	10	45	22.2%
Pu-238	10	105	9.5%
Pu-239	7	105	6.7%
H-3	2	86	2.3%
Sr-90	7	29	24.1%
Non-Natural Gamma	47	962	4.9%
Grand Total	**397**	**3649**	**10.9%**

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Blank Data Discussion

- In general, no significant difference between liquid and solid blanks
  - Exceptions:
    - Uranium Isotopes
      - More rigorous preparation, more reagents, more chance of introducing natural radionuclides
    - Tritium in liquids
    - Sr-90 in Solids
      - Small population of data, possibly just poor statistics

Data

Radionuclides Qualified UJ (detected above L_c) (Since Nov 2019)

Blanks

Analyte	> L_c	N	Percent > L_c
Gross Alpha	6	48	12.5%
Gross Beta	9	47	19.1%
U-234	28	263	10.6%
U-235	29	263	11.0%
U-238	21	263	8.0%
Natural Gamma	271	1854	14.6%
Am-241	26	111	23.4%
Pu-238	16	169	9.5%
Pu-239	11	169	6.5%
H-3	5	99	5.1%
Sr-90	12	72	16.7%
Non-Natural Gamma	60	1234	4.9%

ND Sample Results

Analyte	> L_c	N	Percent > L_c
Gross Alpha	61	208	29.3%
Gross Beta	73	147	49.7%
U-234	14	63	22.2%
U-235	885	1208	73.3%
U-238	37	85	43.5%
Natural Gamma	872	2801	31.1%
Am-241	85	332	25.6%
Pu-238	71	921	7.7%
Pu-239	105	859	12.2%
H-3	63	683	9.2%
Sr-90	55	318	17.3%
Non-Natural Gamma	518	7140	7.3%

Data Discussion

- Am-241 and Sr-90
  - Reported above L_c significantly greater than 5% frequency in method blanks
  - Not significantly different from percentages in non-detected samples
    - More evidence that this appears to be related to laboratory operations
  - So, What can be done?
    - Present data to contract laboratory
    - Work with laboratory to resolve potential issue with reported L_c
    - Validation Qualifiers – significant difference between sample and blank?

Data

Samples Qualified UJ by Matrix (Since Nov 2019)

ND Liquid Sample Results

Analyte	> L_c	N	Percent > L_c
Gross Alpha	61	208	29.3%
Gross Beta	73	147	49.7%
U-234	10	57	17.5%
U-235	62	214	29.0%
U-238	31	72	43.1%
Natural Gamma	46	315	14.6%
Am-241	64	240	26.7%
Pu-238	28	240	11.7%
Pu-239	11	239	4.6%
H-3	6	29	20.7%
Sr-90	34	234	14.5%
Non-Natural Gamma	48	947	5.1%

ND Solid Sample Results

Analyte	> L_c	N	Percent > L_c
Gross Alpha	0	0	0.0%
Gross Beta	0	0	0.0%
U-234	4	6	66.7%
U-235	823	994	82.8%
U-238	6	13	46.2%
Natural Gamma	1648	3467	47.5%
Am-241	21	92	22.8%
Pu-238	43	681	6.3%
Pu-239	94	620	15.2%
H-3	57	654	8.7%
Sr-90	21	84	25.0%
Non-Natural Gamma	468	6184	7.6%

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Summary

- New approach to defining detected radionuclides at N3B-Los Alamos
  1. Aligns with industry standards and guidance documents
  2. Aligns radionuclide detection criteria more closely with standard chemistry methods
  3. Maintains historic definitions of detects for continuity and data comparison
  4. Offers more information to projects and decision makers
  5. Provides better transparency to regulators and public with regard to low-level radionuclide detection
  6. Path forward includes evaluation of critical level calculations used by the lab and if they are appropriate for all measurements (e.g., natural radionuclides)

Reference Documents

- ANSI/ANS-41.5-2012, Verification and Validation of Radiological Data for use in Waste Management and Environmental Remediation.
- NUREG-1576, EPA 402-B-04-001A, NTIS PB2004-105421, Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP).
- LANL Publication, LA-UR-14-27861, Analysis and Recommendations for Defining Detection Status for Radionuclides in Environmental Samples.
- Currie, LA. 1968. Limits for qualitative and quantitative determination-Application to radiochemistry. Analytical Chemistry 40:586-593.
- EPA 821-R16-006, Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.


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