Analytical Protocol Specifications

Analyte List: ⁹⁰Sr

Analysis Limitations: <u>Perform direct measurement of analyte.</u> <u>Analysis of progeny allowed if radioactive equilibrium is established at</u> <u>laboratory from freshly isolated parent.</u>

Possible Interferences: Fresh beta-emitting, fission-product nuclides if

Matrix: Raw Cow's Milk (fat content to vary)

Concentration Range: 1 to 50 pCi/L

Action Level: <u>8 pCi/L</u>

purification steps are inadequate or non-existent.

Method Validation Level: MARLAP Levels A, C, or D as applicable. See Attachment C for details.

MQOs: <u>A required method uncertainty (u_{MR}) of 0.5 pCi/L at the action level of 8 pCi/L and a relative method uncertainty (ϕ_{MR})</u>

of 6.25% at > 8pCi/L

| | QC Samples | |
|---------------------------|-------------|----------------------------|
| Туре | Frequency | Evaluation Criteria |
| Method blank | 1 per batch | See Attachment B |
| Duplicate | 1 per batch | See Attachment B |
| Matrix Spike* | 1 per batch | See Attachment B |
| Laboratory Control Sample | 1 per batch | See Attachment B |

| Analy | Analytical Process Requirements | | | | |
|---|---|--|--|--|--|
| Activity | Special Requirements | | | | |
| Field Sample Preparation and Preservation | Sample size > 3.5 L; Preserve on ice or with 5 mL of 37% formaldehyde / L sample | | | | |
| Sample Receipt and Inspection | Rad survey samples upon receipt. Return sample receipt acknowledgment letter with date of receipt at lab. Cross index list for Sample ID and assigned Lab ID. Visually inspect containers upon receipt to ensure integrity and normal sample appearance. COC documentation applies. | | | | |
| Laboratory Sample Preparation | Take sufficient aliquant of sample after gamma-ray spectrometry analysis (see separate requirements in the gamma spectroscopy APS). Keep 1 liter as backup until analytical results have been approved by project manager. | | | | |
| Sample Dissolution | None | | | | |
| Chemical Separations | Isolate Sr by cation exchange resin or precipitation of Sr from soured or dry-ashed milk. Separation from Ca is essential. Rare earth and Ba scavenging steps are necessary to eliminate possible interferences from fresh fission products. | | | | |
| Preparing Sources for Counting | Final test source mount to accommodate nuclear instrumentation. | | | | |
| Nuclear Counting | Acceptable counting instrumentation includes: Liquid Scintillation Counter, Gas Proportional Counter or Solid State Beta Detector. Detection. Method must discriminate against potential ⁸⁹ Sr interference by physical means and/or calculation. | | | | |
| Data Reduction and Reporting | See Attachment A | | | | |
| Sample Tracking Requirements | Chain-of-Custody | | | | |
| Other - Chemical Yielding | Gravimetric (must have 99% Ca removal) or ⁸⁵ Sr tracer with > 90% Ca removal. | | | | |

* Spiking range provided in Attachment B

Attachment A Data Reduction and Reporting Requirements

Data Reduction

- 1. The measurement of the ⁹⁰Sr in the sample can be based on quantification of ⁹⁰Sr and/or ⁹⁰Y as long as decay and ingrowth of ⁹⁰Y is properly addressed.
- 2. Calculate the gross, net and background count rate, detector efficiency, chemical yield, decay and ingrowth factors for each sample.
- 3. Calculate the activity concentration and associated combined standard uncertainty of the ⁹⁰Sr concentration in pCi/L at the ti,e of sample collection.
- 4. Calculate the sample specific MDC in pCi/L using the detector efficiency and background, count time, decay and ingrowth factors, Sr yield, and sample volume used for the sample.
- 5. Calculate the sample specific critical level pCi/L using the same factors as for the MDC.
- 6. Initial review and approval of data reduction equations shall be established during a desk or onsite audit as part of the lab approval/contracting process.
- 7. No changes in the equations used in data reduction shall be initiated without prior approval of the project manager.

Data Reporting

- 1. For each sample, the following sample specific parameters shall be reported: Batch #, Sample ID, Lab ID, sample collection (reference) date, sample receipt date, estimated (or actual) sample volume received, ⁹⁰Y separation date, count date, cross reference to batch QC samples, SOP used, analyst, data reviewer and report date.
- 2. For each sample, the following sample processing parameters or factors shall be reported: Gross, net, and background count rates, detector efficiency, sample volume processed, ⁹⁰Sr decay factor, ⁹⁰Y ingrowth and decay factors (and separation and count times), and chemical yield factor.
- 3. For each sample the following calculated information shall be reported: ⁹⁰Sr concentration and associated combined standard uncertainty (CSU), critical level, MDC.
- 4. Batch quality control results for the laboratory control sample (LCS), method blank, duplicate sample and matrix spike sample shall be reported with each batch of samples: Reported data shall include:

LCS - calculated sample and prepared spike concentration with associated CSUs, and percent difference between sample result and known values

Duplicate samples - calculated concentrations with associated CSU for both samples, the calculated absolute difference or RPD

Matrix spike - calculated sample and known spike concentration with associated CSUs, and calculated Z-score for the sample results

- 5. A "Narrative" shall be provided with each batch of samples that describes processes used and any problems encountered or discrepancies noted, including the possible effect on the quality of specific results and actions taken to remedy the problem if recurrent.
- 6. Reports shall be provided electronically and as a hard copy. An electronic data format will be provided.

Attachment B Batch Quality Control Sample Evaluation Criteria

A "batch" of samples is defined as 20 or fewer samples not including the QC samples. The results of the batch QC samples shall be evaluated according to the equations provided below. It should be noted that no action is to be taken when a "not-to-exceed" limit stated below is exceeded for an individual sample. However, if trending of the results indicates multiple results or a trend of results exceeds a limit, stop processing samples and take action to identify and correct the root cause of the problem. Sample processing may resume when corrective actions have been shown to be effective in eliminating the cause of the problem. It is expected that the Laboratory's QA officer and project manager shall provide oversight on the sample processing and track the batch QC results.

Laboratory Control Sample

The ⁹⁰Sr spike concentration of an LCS shall be between 10 and 20 pCi/L and the spiking uncertainty should be \leq 5%. The percent deviation (%D) for the LCS analysis is defined as

$$\%D = \frac{SSR - SA}{SA} \times 100\%$$
 1)

where

SSR is the measured result (spiked sample result) and

SA is the spike activity (or concentration) added.

The %D control limit is $\pm 3 \varphi_{MR} \times 100\%$ or $\pm 19\%$. For long-term trending, the %D results should be plotted graphically in terms of a quality control chart with the expected mean %D value of zero.

Duplicate Samples

The acceptance criteria for duplicate analysis results depends on the analyte concentration of the sample, which is determined by the average x of the two measured results x_1 and x_2 .

$$\overline{x} = \frac{x_1 + x_2}{2} \tag{2}$$

When $\overline{x} < 8$, the control limit for the absolute difference $|x_1 - x_2|$ is 4.24 u_{MR} , or 2.1.

When $\bar{x} \ge 8$ pCi/L, the control limit for the *relative percent difference* (RPD), defined as,

$$\operatorname{RPD} = \frac{x_1 + x_2}{\overline{x}} \times 100\%$$
3)

is 4.24 $\phi_{MR} \times 100\%$ or 27 %. For long-term trending, the absolute difference and RPD results should be plotted graphically in terms of a quality control chart with an expected absolute difference and RPD mean values of zero.

Attachment B (Continued) Batch Quality Control Sample Evaluation Criteria

Matrix Spikes

The acceptance criteria for matrix spikes uses the "Z score," defined below, as the test for matrix spikes. The pre-existing activity (or concentration) must be measured and subtracted from the activity measured after spiking as shown in equations 4) and 5). The ⁹⁰Sr spike concentration of a matrix spike shall be between 10 and 20 pCi/L and the spiking uncertainty should be $\leq 5\%$.

$$Z = \frac{SSR - SR - SA}{\varphi_{MR}\sqrt{SSR^2 + \max(SR, UBGR)^2}}$$
(4)

$$Z = \frac{SSR - SR - SA}{0.0625\sqrt{SSR^{2} + \max(SR,8)^{2}}}$$
 5)

where:

- SSR is the spiked sample result,
- SR is the unspiked sample result,
- SA is the spike concentration added (total activity divided by aliquant mass), and max(SR,8) denotes the maximum of SR and 8 pCi/L.

The control limit for Z is set at \pm 3. It is assumed that the uncertainty of SA is negligible with respect to the uncertainty of SSR. For long-term trending, the Z results should be plotted graphically in terms of a quality control chart with a Z value of zero as the expected mean value.

<u>Method Blanks</u> When an aliquant of a blank material is analyzed, the target value is zero. However, the measured value may be either positive or negative. The applicable control limit for blank samples shall be within $\pm 3 u_{MR}$ or ± 1.5 pCi/L. For long-term trending, the blank results should be plotted graphically in terms of a quality control chart with an expected mean value of zero.

Attachment C Method Validation Requirements

Prior to processing any milk samples, the laboratory is required to validate its ⁹⁰Sr in cow's milk radioanalytical method according to the specifications stated in MARLAP Chapter 6. The level of method validation will depend on whether the laboratory has a previously validated method for ⁹⁰Sr in milk (Level A), will modify a previously validated ⁹⁰Sr method for a milk matrix (Level C) or must newly develop or adapt a method for ⁹⁰Sr in cow's milk (Level D). The laboratory shall submit the method validation documentation to the project manager for review and approval prior to the acquisition of a laboratory contract. A summary of the method validation criteria is presented below for the three validation levels.

Level A method validation pertains to a previously validated method for ⁹⁰Sr in milk. No additional testing is required if the method previously has been successfully validated and the available method validation documentation has been reviewed and approved by the project manager. Documentation of method validation should conform to the specifications provided below.

Level C method validation is to be conducted when a validated ⁹⁰Sr method for a non-milk matrix is modified for applicability for the milk matrix, e.g., when the EPA 905 ⁹⁰Sr in water method is modified for use with a milk matrix. A method validation plan should be developed and documented. Validation Level C requires the preparation and analysis of five replicate cowmilk samples (internal performance testing samples) spiked at three different concentrations. For this project the three levels of 1, 10, 20 pCi/L (or within $\pm 15\%$ of the values) should be used in the validation process. Each sample result for the lowest level (below the action level) must be within $\pm 2.9 u_{MR}$ or ± 1.45 pCi/L of the spiked concentration value. Each sample result from the two higher spiked levels (above the action level) must be within $\pm 2.9 \varphi_{MR} \times 100\%$ or $\pm 18\%$ of the spiked concentration value. Documentation of method validation should conform to the specifications provided below.

Level D method validation is to be conducted when a new method is specifically developed or adapted from the literature for the project's ⁹⁰Sr in milk application. Validation Level D requires the preparation and analysis of seven replicate cow's milk samples (internal performance testing samples) spiked at three different concentrations. For this project the three levels of 1, 10, 20 pCi/L (or within \pm 15% of the values) should be used in the validation process. Each sample result for the lowest level (below the action level) must be within \pm 3.0 u_{MR} or \pm 1.5 pCi/L of the spiked concentration value. Each sample result from the two higher spiked levels (above the action level) must be within \pm 3.0 MR \times 100% or \pm 19% of the spiked concentration value. Documentation of method validation should conform to the specifications provided below.

Method Validation Documentation

Documentation to be submitted to the project manager includes: Method Validation Plan, Method Number, Analyst(s) analyzing the samples, spiked concentration values, experimental results and comparison to the acceptable performance criteria for the validation level.

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RADIOACTIVITY SOLUTIONS

Data Report for: Sample Matrix: Date Samples Received: XYZ Nuclear Handlers, Incorporated Whole Milk April 18, 2006

| Sample | | Analysis | | | | L _c | |
|---------------|---------|----------|-----------|------------------|--------------------------|----------------|--|
| Name – | Sample | Start | Analysis | | Activity $\pm 1\sigma$, | MDC, | |
| Lab ID | Date | Time | Completed | Analyte | pCi/L | pCi/L | |
| Guernsey 1 | 3/24/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 1.61 ± 0.38 | 0.38 | |
| 051002 | 5/24/05 | 4/4/03 | 4/11/03 | 51 | 1.01 ± 0.38 | 0.80 | |
| Jersey 5 | 3/24/05 | 4/4/05 | 4/07/05 | ⁹⁰ Sr | 0.52 ± 0.36 | 0.54 | |
| 051003 | 5/24/05 | 4/4/03 | 4/07/03 | 51 | 0.32 ± 0.30 | 1.2 | |
| Holstein 3 | 3/24/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 1.10 ± 0.37 | 0.33 | |
| 051004 | 5/24/05 | 4/4/03 | 4/11/03 | 51 | 1.10 ± 0.37 | 0.68 | |
| Guernsey 6 | 3/24/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | -0.55 ± 0.93 | 0.22 | |
| 051005 | 5/24/05 | 4/4/03 | 4/11/03 | 51 | -0.33 ± 0.93 | 0.50 | |
| Jersey 8 | 3/25/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 1.55 ± 0.37 | 0.30 | |
| 051006 | 5/25/05 | 4/4/03 | 4/11/03 | 51 | 1.55 ± 0.57 | 0.61 | |
| | | | | | | | |
| Guernsey 1 DU | 4/4/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 1.95 ± 0.38 | 0.41 | |
| 051008 | 4/4/03 | 4/4/03 | 4/11/03 | 51 | 1.93 ± 0.38 | 0.85 | |
| Batch Blank | 4/4/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | -0.43 ± 0.66 | 0.62 | |
| 051009 | 4/4/03 | 4/4/03 | 4/11/03 | 51 | -0.43 ± 0.00 | 1.3 | |
| LCS | 4/4/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 12.81 ± 0.49 | 0.69 | |
| 051007 | 4/4/03 | 4/4/03 | 4/11/03 | 51 | 12.01 ± 0.49 | 1.5 | |
| Jersey 8 MS | 1/1/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 15 50 + 0 51 | 0.79 | |
| 051010 | 4/4/05 | 4/4/05 | 4/11/05 | 51 | 15.50 ± 0.51 | 1.6 | |

Matrix Spike: 20.0 pCi/L added.

LCS Target: 10.0 pCi/L

Analysis by Liquid Scintillation Counting

Critical Level and Minimum Detectable Concentration values are sample specific

Approved by: I. M. Wright, QA Officer



RADIOACTIVITY SOLUTIONS

Data Report for: Sample Matrix: Date Samples Received: XYZ Nuclear Handlers, Incorporated Whole Milk April 18, 2006

| Sample Name – Lab ID Guernsey 1 | Sample Date | Analysis Start Time | Analysis Completed | Analyte | Activity ± 1σ, pCi/L | L _c MDC, <u>pCi/L</u> 0.38 | Initial Data Qualifiers |
|--|----------------|---------------------------|-----------------------|------------------|-------------------------|--|----------------------------|
| 051002 | 3/24/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 1.61 ± 0.38 | 0.38 0.80 0.54 | |
| Jersey 5 051003 | 3/24/05 | 4/4/05 | 4/07/05 | ⁹⁰ Sr | 0.52 ± 0.36 | 1.2 | |
| Holstein 3 051004 | 3/24/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 1.10 ± 0.37 | 0.33 0.68 | |
| Guernsey 6 051005 | 3/24/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | -0.55 ± 0.93 | 0.22 0.50 | |
| Jersey 8 051006 | 3/25/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 1.55 ± 0.37 | 0.30 0.61 | |
| | | | | | | | |
| Guernsey 1 DU 051008 | 4/4/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 1.95 ± 0.38 | 0.41 0.85 | |
| Batch Blank 051009 | 4/4/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | -0.43 ± 0.66 | 0.62 1.3 | |
| LCS 051007 | 4/4/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 12.81 ± 0.49 | 0.69 1.5 | |
| Jersey 8 MS 051010 | 4/4/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 15.50 ± 0.51 | 0.79 1.6 | |

Matrix Spike: 20.0 pCi/L added.

LCS Target: 10.0 pCi/L

Analysis by Liquid Scintillation Counting

Critical Level and Minimum Detectable Concentration values are sample specific

Approved by: I. M. Wright, QA Officer



RADIOACTIVITY SOLUTIONS

Data Report for: Sample Matrix: Date Samples Received: XYZ Nuclear Handlers, Incorporated Whole Milk April 18, 2006

| Sample | | Analysis | | | | L _c | |
|---------------|---------|----------|-----------|------------------|-------------------|----------------|-------------------------|
| Name – | Sample | Start | Analysis | | Activity <u>+</u> | MDC, | Final |
| Lab ID | Date | Time | Completed | Analyte | lσ, pCi/L | pCi/L | Qualifiers |
| Guernsey 1 | 3/24/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 1.61 ± 0.38 | 0.38 | S(+,-) |
| 051002 | 5/24/05 | 4/4/03 | 4/11/03 | 51 | 1.01 ± 0.38 | 0.80 | |
| Jersey 5 | 3/24/05 | 4/4/05 | 4/07/05 | ⁹⁰ Sr | 0.52 ± 0.36 | 0.54 | S(+,-), U |
| 051003 | 3/24/05 | 4/4/05 | 4/07/03 | 51 | 0.32 ± 0.30 | 1.2 | |
| Holstein 3 | 2/24/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 1 10 + 0 27 | 0.33 | S(+,-) |
| 051004 | 3/24/05 | 4/4/05 | 4/11/05 | Sr | 1.10 ± 0.37 | 0.68 | |
| Guernsey 6 | 2/24/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 0.55 + 0.02 | 0.22 | S(+,-), U, Q |
| 051005 | 3/24/05 | 4/4/05 | 4/11/05 | Sr | -0.55 ± 0.93 | 0.50 | |
| Jersey 8 | 2/25/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 1.55 + 0.27 | 0.30 | S(+,-) |
| 051006 | 3/25/05 | 4/4/05 | 4/11/05 | 51 | 1.55 ± 0.37 | 0.61 | |
| | | | | | | | QC Test |
| | | | | | | | Qualifiers ¹ |
| Guernsey 1 DU | 4/4/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 1.95 ± 0.38 | 0.41 | |
| 051008 | 4/4/05 | 4/4/05 | 4/11/05 | 51 | 1.95 ± 0.38 | 0.85 | |
| Batch Blank | 4/4/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 0.42 ± 0.00 | 0.62 | U |
| 051009 | 4/4/05 | 4/4/05 | 4/11/05 | 51 | -0.43 ± 0.66 | 1.3 | C |
| LCS | 1/1/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 12 01 + 0.40 | 0.69 | S (+) |
| 051007 | 4/4/05 | 4/4/05 | 4/11/05 | Sr | 12.81 ± 0.49 | 1.5 | |
| Jersey 8 MS | 4/4/05 | 4/4/05 | 4/11/05 | ⁹⁰ Sr | 15 50 + 0 51 | 0.79 | S (-) |
| 051010 | 4/4/05 | 4/4/05 | 4/11/05 | Sr | 15.50 ± 0.51 | 1.6 | |

Matrix Spike: 20.0 pCi/L added.

LCS Target: 10.0 pCi/L

Analysis by Liquid Scintillation Counting

Critical Level and Minimum Detectable Concentration values are sample specific

Approved by: I. M. Wright, QA Officer

*The grayed-out qualifiers in the final column (E, Q) are present only as part of this exercise. These qualifiers generally would NOT be applied to the QC samples. This is particularly true for the matrix spike and the LCS where the MDC is relatively unimportant when the measured concentraiton is obviously real. The E that was added in the sample section indicates that the MDC required in the APS of 1.0 pCi/L was not met. In this case, the E may or may not be retained by the data validator.

Data Qualifiers

(MARLAP Chapter 8, Section 8.3.3)

Qualifiers Applied During Verification

E Indicates that an exception or noncompliance has occurred. (This qualifier may be removed during the validation if evidence shows that this exception does not affect the sample results.)

Qualifiers Applied to Samples During Validation Based on Sample Results

- U Analytical result is less than the critical value; a nondetect.
- **Q** A reported measurement uncertainty that exceeds the required method uncertainty or relative method uncertainty (ϕ_{MR} or u_{MR}).
- J A result that is unusually uncertain or estimated.
- **R** A result that is rejected due to severe data problems.

Qualifiers Applied to Samples During Validation Based on QC Sample Results

- S(+/-) A LCS, MS, or MSD that is above (+) or below (-) the upper or lower control limit.
- **P** A sample result with its duplicate (replicate) that exceeds a control limit.
- B(+/-) A blank result that is outside the upper (+) or lower (-) control limit.

Laboratory XYZ



"We are the Wizards"

| Project Name: | Plutonium Fabricators, Ltd |
|----------------------|---|
| Sample Date: | September 1, 2005 |
| Analysis Date: | November 1, 2005 |
| Analysis Method: | Alpha Spectrometry, Method W04, ²⁴¹ Am |
| <u>QC Batch ID:</u> | 200407-123 |

| | | Sample Result | lσ CSU | | |
|--------------|---------------|---------------|---------|----------------|-----------|
| Client ID | Laboratory ID | (pCi/L) | (pCi/L) | L _c | Qualifier |
| 090105W1 | 1885P001 | -0.02 | 0.61 | 0.28 | |
| 090105W2 | 1885P002 | 4.97 | 0.50 | 0.24 | |
| 090105W3 | 1885P003 | 1.18 | 0.26 | 0.12 | |
| 090105W4 | 1885P004 | 12.61 | 0.71 | 0.32 | |
| 090105W5 | 1885P005 | -0.10 | 1.7 | 0.83 | |
| 090105W6 | 1885P006 | 22.6 | 1.1 | 0.55 | |
| 090105W7 | 1885P007 | -0.2 | 1.0 | 0.48 | |
| 090105W8 | 1885P008 | 6.66 | 0.57 | 0.21 | |
| 090105W9 | 1885P009 | 1.55 | 0.38 | 0.16 | |
| 090105W10 | 1885P010 | 0.9 | 1.6 | 0.75 | |
| Matrix spike | 1885PMS1-P002 | 36.1 | 1.1 | 0.60 | |
| LCS | 1885PQC1 | 26.1 | 1.0 | 0.48 | |
| Blank | 1885PB1 | 4.0 | 1.6 | 0.69 | |
| Duplicate | 1885PDP1-P008 | 11.66 | 0.70 | 0.38 | |

Spike added to sample 1885P002 = 24.0 pCi/L
 LCS spike added value = 20.0 pCi/L

I. For the Matrix Spike Result.

Calculate the "Z statistic" using the following equation:

$$Z = \frac{SSR - SR - SA}{\varphi_{MR} \times \sqrt{SSR^2 + \max(SR, AL)^2}}$$

SSR: Spiked sample result =

- SR: Unspiked sample result =
- SA: Spike concentration added =
- φ_{MR} : Required *relative* method uncertainty above the action level (AL) expressed as a fraction: $\varphi_{MR} = [u_{MR} / AL] =$
 - (1) SSR: _____- SR: _____ SA: ____ = ____ (2) SSR²: _____ + max(SR, AL):(_____)² = _____ (3) [from 2] $\frac{1}{2}$ = _____ × φ_{MR} = _____ = ____ (4) [from 1]: _____ / [from 3]: _____ = Z: _____

II. Calculate the %D for the Laboratory Control Sample Using the Following Equation:

$$\%D = 100\% \times \frac{SSR - SA}{SA}$$

- SA: Spike concentration added as LCS = _____
 SSR: Measured Concentration of the LCS = _____
- (3) SSR: SA: = = (4) %D = 100% [from 3] / [from 1] = =

Calculate the Control Limit % from:

 $CL = 3 \times \phi_{MR} \times 100\% = 3 \times ___ \times 100\% =$

III. For the Duplicate Result

Calculate the agreement based on the absolute value of the average of the two results as compared with the AL:

 $\begin{array}{c} x_{1}: \underline{\qquad} \\ x_{2}: \underline{\qquad} \\ AL: \underline{\qquad} \\ MR: \underline{\qquad} \\ x_{avg} = \left| x_{1} + x_{2} \right| / 2 = \left| \underline{\qquad} + \underline{\qquad} \right| / 2 = \left| \underline{\qquad} \right| \\ If x_{avg} > AL \text{ then use} \\ Control Limit = 4.24 \times \varphi_{MR} \times 100 = 4.24 \times \underline{\qquad} \times 100 = \\ \underline{\qquad} \\ and \text{ compare the relative percent difference to the CL:} \end{array}$

$$\text{RPD} = 100 \times \frac{|\mathbf{X}_2 - \mathbf{X}_1|}{\mathbf{X}_{\text{avg}}}$$

If $x_{avg} < AL$ then use

Control Limit = $4.24 \times u_{MR} = 4.24 \times ___= ___$ and compare the absolute difference to the CL: Absolute difference = $|x_2 - x_1| = |____= __= |= ____$

IV. For the Laboratory Blank Sample:

The control limit for the blank distribution is given by:

Control Limit = $3 \times u_{MR} = 3 \times ($ ____) = ____

The value for the blank is compared to this limit.

The Key to the MARLAP Process

The principal MQOs in any project will be defined by:

- The *required method uncertainty*, u_{MR} , below the *action level*
- The *relative method uncertainty*, ϕ_{MR} , above the *action level*

$\varphi_{\rm MR} = u_{\rm MR} / \rm{AL}$

When making decisions about *individual samples* $u_{MR} \sim \Delta/3$

When making decisions about the *mean of several samples* . . $u_{MR} \sim \Delta/10$

Where Δ is the width of the gray region $\Delta = AL - DL$

Method Uncertainty: MARLAP's Common Thread

Definition:

- Predicted uncertainty of a measured value that would likely result from the analysis of a sample at a specified analyte concentration.
- · Combines imprecision and bias into a single parameter whose interpretation does not depend on context.

MARLAP recommends:

- Identify the method uncertainty at a specified concentration (typically the *action level*) as an important method performance characteristic.
- Establish a measurement quality objective for method uncertainty for each analyte/matrix combination.

MQO for the method uncertainty (at a specified concentration):

- Links the three phases of the data life cycle: planning, implementation, and assessment.
- Related to the width of the gray region. The gray region has an upper bound and a lower bound. The upper bound typically is the <u>action level</u>, and the lower bound is termed the "<u>discrimination limit</u>."

Examples of MQOs for method uncertainty at a specified concentration:

- A method uncertainty of 0.01 Bq/g or less is required at the action level of 0.1 Bq/g.
- The method must be able to quantify the amount of ²²⁶Ra present, given elevated levels of ²³⁵U in the samples.

Terminology:

- *u*_{MR} Required method uncertainty (absolute)
- $\varphi_{MR} = u_{MR} / AL$ Required method uncertainty (relative)
- $\Delta = AL DL$ Width of the gray region (range of values where the consequences of a decision error are relatively minor)
- Action level Concentration that will cause a decisionmaker to choose one of the alternative actions
- Discrimination limit Synonymous with the lower bound of the gray region

I. For the Matrix Spike Result.

Calculate the "Z statistic" using the following equation:

| z - SSR - S | R - SA |
|---|-----------------|
| $\mathcal{L} = \frac{1}{\varphi_{_{\mathrm{MR}}} \times \sqrt{\mathrm{SSR}^2 + 1}}$ | $\max(SR,AL)^2$ |
| SSR: Spiked sample result = | 36.1 pCi/L |
| SR: Unspiked sample result = | 4.97 pCi/L |
| SA: Spike concentration added = | 24.0 pCi/L |

 φ_{MR} : Required *relative* method uncertainty above the action level (AL) expressed as a fraction: $\varphi_{MR} = [u_{MR} / AL] = 0.98/15 \text{ pCi/L} = 0.065 \text{ or } 6.5\%$

| (1) | SSR: <u>36.1</u> - SR: <u>4.97</u> - SA: <u>24.0</u> | = | 7.13 pCi/L |
|-----|--|---|-------------|
| (2) | $SSR^{2}:$ <u>1303</u> + max(SR, AL):(<u>225</u>) ² | = | 1528.21 |
| (3) | $[\text{ from 2}]^{\frac{1}{2}} = \underline{39.09} \times \phi_{MR} = \underline{39.09} \times 0.065$ | = | 2.541 pCi/L |
| (4) | [from 1]: <u>7.13</u> / [from 3]: <u>2.541</u> | = | Z: 2.81 |

II. Calculate the %D for the Laboratory Control Sample Using the Following Equation:

$$\%D = 100\% \times \frac{SSR - SA}{SA}$$

| (1) | SA: Spike concentration added as LCS | = | 20.0 pCi/L |
|-----|---|---|------------|
| | SSR: Measured Concentration of the LCS | = | 26.1 pCi/L |
| | | | 6.1 pCi/L |
| (4) | %D = $\overline{100\% \text{ [from 3]} / \text{ [from 1]}}$ | = | 30.5% |

Calculate the Control Limit % from:

$$CL = 3 \times \phi_{MR} \times 100\% = 3 \times \phi_{MR} \times 0.98 \times 100\% = 19.5\%$$

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III. For the Duplicate Result

Calculate the agreement based on the absolute value of the average of the two results as compared with the AL:

 $\begin{array}{l} x_{1}: & \underline{6.66 \ pCi/L} \\ x_{2}: & \underline{11.66 \ pCi/L} \\ AL: & \underline{15} \\ u_{MR}: \ 0.98 \ pCI/L \end{array}$

 $x_{avg} = |x_1 + x_2|/2 = |\underline{6.66} + \underline{11.66}|/2 = -\underline{9.16}| = \underline{9.16} \text{ pCi/L}$

If $x_{avg} > AL$ then use

Control Limit = $4.24 \times \phi_{MR} \times 100\% = 4.24 \times 0.065 \times 100\% = 27.6\%$ and compare the relative percent difference to the CL:

RPD =
$$100 \times \frac{|\mathbf{x}_2 - \mathbf{x}_1|}{(\mathbf{x}_1 + \mathbf{x}_2)/2}$$

If $X_{avg} < AL$ then use

Control Limit = $4.24 \times u_{MR} = 4.24 \times 0.98 = 4.15$ pCi/L compare the absolute difference to the CL: Absolute difference = $|x_2 - x_1| = |\underline{6.66} - \underline{11.66}| = 5.00$ pCi/L

IV. For the Laboratory Blank Sample:

The control limit for the blank distribution is given by:

Control Limit =
$$\pm 3 \times u_{\text{MR}} = \pm 3 \times (0.98) = \pm 2.94 \text{ pCi/L}$$

The value for the blank is compared to this limit.

Laboratory XYZ



"We are the Wizards"

| Project Name: | Plutonium Fabricators, Ltd |
|------------------|---|
| Sample Date: | September 1, 2005 |
| Analysis Date: | November 1, 2005 |
| Analysis Method: | Alpha Spectrometry, Method W04, ²⁴¹ Am |

| | | Sample Result | lσ CSU | | |
|--------------|----------------------------|---------------|---------|----------------|-----------|
| Client ID | Laboratory ID | (pCi/L) | (pCi/L) | L _c | Qualifier |
| 090105W1 | 1885P001 | -0.02 | 0.61 | 0.28 | U,P |
| 090105W2 | 1885P002 | 4.97 | 0.50 | 0.24 | B+,S+,P |
| 090105W3 | 1885P003 | 1.18 | 0.26 | 0.12 | B+,S+,P |
| 090105W4 | 1885P004 | 12.61 | 0.71 | 0.32 | B+,S+,P |
| 090105W5 | 1885P005 | -0.10 | 1.7 | 0.83 | Q,U,P |
| 090105W6 | 1885P006 | 22.6 | 1.1 | 0.55 | B+,S+,P |
| 090105W7 | 1885P007 | -0.2 | 1.0 | 0.48 | U,P |
| 090105W8 | 1885P008 | 6.66 | 0.57 | 0.21 | B+,S+,P |
| 090105W9 | 1885P009 | 1.55 | 0.38 | 0.16 | B+,S+,P |
| 090105W10 | 1885P010 | 0.9 | 1.6 | 0.75 | Q,B+,S+,P |
| Matrix spike | 1885PMS1-P002 ¹ | 36.1 | 1.1 | 0.60 | |
| LCS | 1885PQC1 ² | 26.1 | 1.0 | 0.48 | S+ |
| Blank | 1885PB1 | 4.0 | 1.6 | 0.69 | Q,B+ |
| Duplicate | 1885PDP1-P008 | 11.66 | 0.70 | 0.38 | P |

Spike added to sample 1885P002 = 24.0 pCi/L
 LCS spike added value = 20.0 pCi/L