Analytical Protocol Specifications

Analyte List: ^{90}Sr

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

Matrix: Raw Cow's Milk

Possible Interferences: Fresh beta-emitting, fission-product nuclides if purification steps are inadequate or non-existent.

Concentration Range: 1 to 50 pCi/L

Action Level: 8 pCi/L

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

MQOs: A required method uncertainty (u_{MR}) of 0.5 pCi/L at 8 pCi/L and a relative method uncertainty (φ_{MR}) of 6.25% at > 8pCi/L

QC Samples		
Type	**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

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	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. Rad survey samples upon receipt. 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	Isolation of Sr from the milk by either cation 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 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 to discriminate to the extent possible for potential ^{89}Sr contamination by physical or calculations means.
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. Calculation of Sr-90 activity or concentration (pCi/L) can be based on the quantification of Sr-90 and/or Y-90, with proper addressing of decay and ingrowth of Y-90.
2. Calculation of the associated combined standard uncertainty (pCi/L) of the ^{90}Sr concentration.
3. Calculation of the MDC, in terms of pCi/L, shall be sample specific using the detector efficiency and background, counting time, decay and ingrowth factors, Sr yield and sample volume used for the analysis.
4. Calculation of critical level, in terms of pCi/L, shall be sample specific.
5. Calculation of gross, net and background count rate, detector efficiency, chemical yield, decay and ingrowth factors for each sample.
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, ^{90}Y separation date, counting 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, ^{90}Sr decay factor, ^{90}Y decay and ingrowth factors (and times), and chemical yield factor.
3. For each sample the following calculated information will be reported:
   critical level, MDC, ^{90}Sr concentration and associated combined standard uncertainty (CSU).
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:
   Reporting data to include:
   LCS - calculated sample and prepared spike concentration with associated CSUs, and percent difference between sample result and known value
   Duplicate samples - calculated concentrations with associated CSU for both samples
   Matrix spike - calculated sample and known spike concentration with associated CSUs, and percent difference between sample results
5. A “Narrative” shall be provided with each batch of samples that describes problems encountered or noted discrepancies for any sample, possible effect on the quality of a result 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 samples or less 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 indicate many results or a trend of results exceeds a limit, actions must be taken to stop processing samples, identify the root cause of the problem and take corrective actions. Sample processing can resume when the 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 shall track the batch QC results.

Laboratory Control Sample

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

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

where

SSR is the measured result (spiked sample result) and
SA is the spike activity (or concentration) added.

The %D control limit is ± 3 φ_{MR} × 100% or ±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 criterion for duplicate analysis results depends on the analyte concentration of the sample, which is determined by the average $\bar{x}$ of the two measured results x_1 and x_2.

$$\bar{x} = \frac{x_1 + x_2}{2} \qquad 2)$$

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

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

$$\text{RPD} = \frac{x_1 + x_2}{\bar{x}} \times 100\% \qquad 3)$$

is 4.24 φ_{MR} × 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. The ^{90}Sr spike concentration of a matrix spike shall be between 10 and 20 pCi/L and the spiking uncertainty should be ≤ 5%.

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

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

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 ± 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.

Method Blanks 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 ± 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 ^{90}Sr in 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 ^{90}Sr in milk (Level A), will modify a previously validated ^{90}Sr method for a milk matrix (Level C) or must newly develop or adapt a method for ^{90}Sr in 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 ^{90}Sr 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 ^{90}Sr method for a non-milk matrix is modified for applicability for the milk matrix, e.g., when the EPA 905 ^{90}Sr 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 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 ± 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 ± 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 ± 2.9 $\varphi_{MR} \times 100\%$ or ± 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 ^{90}Sr in milk application. Validation Level D requires the preparation and analysis of seven replicate 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 ± 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 ± 3.0 u_{MR} or ± 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 ± 3.0 $\phi_{MR} \times 100\%$ or ± 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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