Evaluating Methods and Laboratories

Module 9

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Overview

This section of MARLAP examines:

- Proposed method evaluation
- Laboratory selection

Proposed Analytical Method

Needs to satisfy:

- Measurement Quality Objectives (MQOs)
- Method validation requirements
- Regulatory requirements
- Data deadlines
- Project costs

Proposed Method Evaluation

Proposed method should not be based on:

- Previously identified methods for the same analyses

- Capricious request for the "best" method

- The only method that a particular laboratory has for the analysis

How Many Methods Are Needed?

	Soil	Concrete	Water	Grass
^{90}Sr	★			★
^{137}Cs	★		★	
^{14}C				
^{3}H	★	★		

Method Evaluation (7.2.2)

- Technical evaluation committee (TEC) or radioanalytical specialist considers whether proposed method is appropriate based on project requirements
- What considerations affect method evaluation?
  - MQOs
  - Radiological holding time (during transport and in the laboratory)
  - Preservation or storage techniques
  - Sample digestion
  - Interferences, both radiological and non-radiological (more or less significant)
  - Turnaround time for results
  - Method bias (see MARLAP Attachment 6A)

Deciding on a Method

TEC & Project Manager decide that the methods proposed by the laboratory are:

- Appropriate
  - Can achieve the MQOs and other APS requirements

- Not appropriate
  - Cannot achieve the MQOs or other APSs

What Methods Meet the ^{90}Sr MQOs?

^{90}Sr Example MQO:
A method uncertainty (u_{MR}) of 0.5 pCi/L or less at 8 pCi/L

	LSC	Beta Detector	GPC	Required for Project
Routine Method Uncertainty (pCi/L)	0.2	1.0	0.3	0.5 (**Required Method Uncertainty**)

Laboratory Evaluation Process

Laboratory evaluation process follows the evaluation and approval of the method by the TEC:

- Initial
- Continuing

Laboratory Evaluation Process (7.3)

Consider:

- Quality manual
- Staff, instrumentation, and facilities
- Prior contract work
- Performance of internal QC program
- Performance in external proficiency evaluation programs

Continued…

Laboratory Evaluation Process (7.3)

Continued…

- Is an onsite audit or assessment necessary?
- Can audit reports from other entities be used?
- Proficiency test/evaluation samples as a pre-award requirement?
- Is the laboratory accredited? By whom?

Which Laboratory to Select?

- The method is accepted by the TEC
- The laboratory is approved based on the laboratory's quality program, external audits, staffing, etc.
- Several laboratories may meet the requirements
- The scoring and evaluation scheme* developed will allow the PM to decide which laboratory to select

Technical Evaluation Scheme Example

Element	Description	Weight (%)
I	Technical Merit	25
II	Past Performance	25
III	Understanding of the Requirements	15
IV	Adequacy and Suitability of Proposed Equipment and Resources	15
V	Academic Qualifications and Experience of Personnel	10
VI	Related Experience	10

Ongoing Evaluation of Laboratory Performance (7.4)

- Project plan should identify the method of ongoing evaluation, using the Statement of Work (SOW) and APS as a quantitative measure:
  - "Desk" audit (using data packages from laboratory)

and if necessary

  - Onsite audit

- Evaluation of QC samples for all matrices is a major part of either type of audit.

Key Laboratory Quality Control Samples

In the MARLAP process, the criteria for evaluating the batch QC samples are based on the required project-specific method uncertainty

- Matrix spike
- Laboratory control sample (LCS)
- Duplicate sample
- Laboratory blank
- Matrix spike duplicate

Why Do All These QC samples?

- To help ensure data is of proper quality to support the decision
- The purpose of trending method uncertainties, LCS, and spike results is to help decide if methods or laboratories need to be changed.
- This is part of the feedback loop for confirmation of performance/improvement in the MARLAP process
- *…and because the regulators tell you to*

Matrix Spike

- Acceptable spiking range
- Method of spiking
- Acceptance criteria (Z score)

Matrix Spike Requirements for ^{90}Sr in Milk

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

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

Control limits for Z statistic are ±3

Spike added is 50 pCi/L. Spiked sample result is 57.8 pCi/L. Unspiked sample result is 4 pCi/L. Does this meet the APS requirements?

Laboratory Control Sample

- Usually made in demineralized water matrix for liquids (this would be the case for milk, unless a surrogate, synthetic matrix is specified in the SOW)

- Activity concentration should be near the AL

- The uncertainty of the spike activity used is normally negligible

LCS QC Requirements for ^{90}Sr in Milk

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

SSR = Spiked sample result

SA = spike activity (or concentration) added

Control limits: $(\pm 3\ \varphi_{MR}) \times 100$

Note that limits are in %

Would an LCS value of 12.0 pCi/L be an acceptable result for our example if the LCS Expected value is 10 pCi/L?

Duplicate Sample

- A second aliquant taken from the original sample container

- Agreement based on a statistical test when average of both samples is within a specified range

Duplicates QC Requirements for ^{90}Sr in Milk

$$\overline{X} = \frac{X_1 + X_2}{2}$$

When $\overline{X} < 8$ the control limit for the absolute difference $|x_1 - x_2|$ is

$$CL = 4.24\, u_{MR} = 4.24 \times 0.5 = 2.1$$

When $\overline{X} > 8$ the control limit for the *relative percent difference (RPD)* is

$$RPD = 100 \times \frac{|x_1 - x_2|}{\overline{X}}$$

and the value for the limit is

$$CL = 4.24\, \varphi_{MR} \times 100 = 4.24 \times 0.0625 \times 100 = 27\%$$

Duplicate results are obtained on an unknown sample: 14.6 and 17.2 pCi/L. Are they acceptable per our example APS?

Blanks

How are they made?

- Field blank
- Trip blank
- Method blank

Actions if blanks are "positive" for activity?

- Repeat batch analysis?
- Subtract blank value from all results?

Batch Blank Sample QC Requirements for ^{90}Sr in Milk

Ideally the "true" value is zero. Control chart should have the central line at zero with:

Control limits: $\pm 3\ u_{MR}$

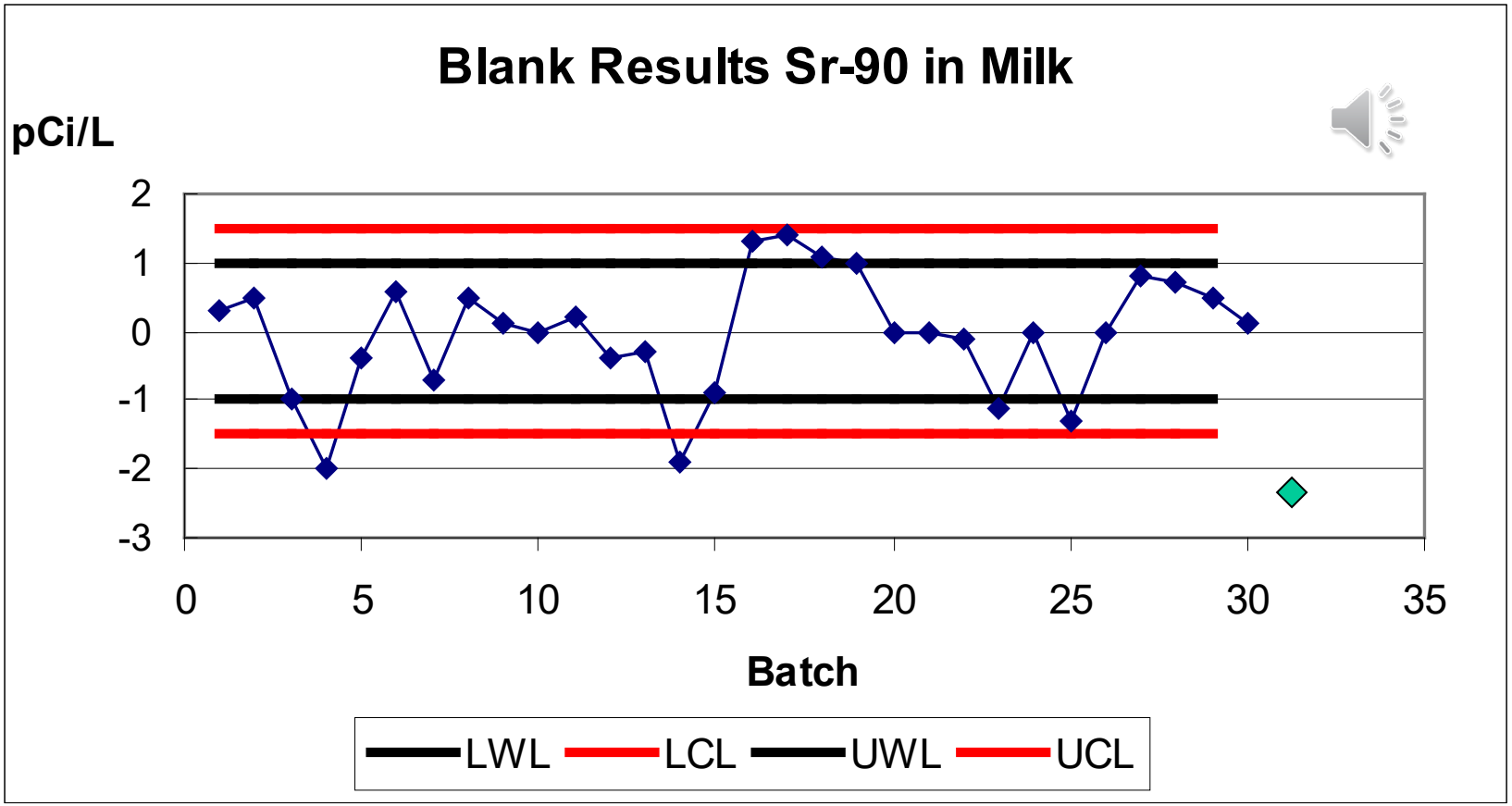
Values plotted on the control chart for trending

No action based on single measurement

Control limit for Sr APS is 1.5 pCi/L (3 × 0.5 pCi/L)

See example on next slide

EXAMPLE:
QC Requirements - ^{90}Sr in Milk



The current value ◇ for your batch is –2.2. OK?

Stipulation of Quality Control
APS for ^{90}Sr in Milk

- What is the significance of the Attachment B "preamble" of the APS*?

- Note the specificity of agreement criteria for each of the QC samples.

See handout

MARLAP Recommends…

- Radioanalytical specialist reviews the methods for technical adequacy
- TEC performs an independent calculation of the method's MDC and required method uncertainty (u_{MR}) using laboratory's typical or sample-specific parameters
- PM or TEC evaluates available lab data for bias based on proficiency testing of samples
- "Z-score" is used for matrix spike evaluation
- An audit team include a radioanalytical specialist

Practice Activity

The pdf document "Lab results Samples and QC Sr90 in Milk" provide the laboratory control charts for the first 30 batches of samples analyzed for 90Sr in milk. The third page provides the analytical results for your milk samples in batch #31.

Using the information provided

1. Determine if the QC samples measured in batch #31 set are within control limits
2. Has the laboratory met the most important MQO for each sample analyzed?
3. Provide a critical assessment of the historical QC record for this laboratory, indicating if any follow up or corrective actions are required.

Your Answers

- Write your answers to the questions on the previous slide On a piece of paper or in a word file before continuing to the next slide.

Answers (part 1 of 4)

- For the duplicate samples the values are 1.61 and 1.95 for an average of 1.78 pCi/L. This is below the AL so the formula to be used is the absolute difference between the two values: this is 0.34. For this example we had calculated that the control limit was 2.1 pCi/L (see slide 22). *The duplicate result is acceptable.*
- The value for the batch blank was -0.43 pCi/L. On slide 24 we calculated the Blank QC limit as 0 ± 1.5 pCi/L. *The blank result is acceptable.*

Answers (part 2 of 4)

- The formula for determining the LCS limits is found on slide 20. For a 10 pCi/L LCS, the φ_{MR} value is the fraction 0.0625. This is multiplied by ten and then 3 to get the control limits of 10 ± 1.88 pCi/L The value shown in the laboratory report is 12.81 pCi/L. *The LCS result is not acceptable*.

- The formula for calculating the Z-value for the matrix spike is given on slide 18. Using that formula the Z value for the matrix spike sample result is -5.54
  The control limit of the Z-value is ± 3. *The MS result is not acceptable.*

Answers (part 3 of 4)

- The most important MQO for this project is the required method uncertainty. The value decided upon by the project team was 0.5 pCi/L The measurement uncertainty for each sample was to be less than 0.5 pCi/L for all samples less than the action level, and less than 6.25 % for all sample results above the action level. Guernsey 6 and the batch blank have measurement uncertainties greater than this value. A notation must be made in the report to the project team regarding this lack of achieving a project MQO on samples or QCs.

Answers (part 4 of 4)

Statistically based control charts with limits at ± 2σ and ± 3 σ normally should have values that exceed these limits 5 % and 0.3 % of the time. This is to be expected. Occurrences of exceeding these limits greater than those percentages, should cause a laboratory to investigate why it is happening.

Each control chart is greater than these expected limits. Additionally, the duplicate appears to have a cyclic pattern, the LCS has a positive bias and the matrix spike a negative bias. An on-site audit would be recommended for this laboratory and all analytical work for the project should cease until the audit is complete.

QC	Number Exceeds 2σ	% Exceeds	Number Exceeds 3σ	% Exceeds
LCS	8	26	3	10
Blank	5	16	3	10
Duplicate	4	13	3	10
Matrix spike	3	10	1	3