Radiochemical Data Verification and Validation

Module 10

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What is Data Verification?

- Laboratory conditions and operations are compliant with:
  - SOW
  - Sample analysis plan
  - Quality assurance project plan (QAPP)
- Identifies problems that should be investigated during data validation
  - Checks for consistency and *comparability* of the data throughout the data package
  - Checks for *completeness* of the results to ensure all necessary documentation is available
- Verifies material was delivered by the laboratory in compliance with SOW

Data Verification

Focuses on the individual data generated by the laboratory for each sample and laboratory process:

- Are the data calculation processes and analytical methods *compliant* with the SOW?
- Based on measurable factors
- Verification report presents summary of the process including a single data qualifier (**E**) if needed

Data Verification
(*Continued*)

Verification determines whether:

- Correct procedures were used
- All required documentation was included in the laboratory report.
- The report conforms to requirements in the SOW
- Requirements for MDC or method uncertainty (u_{MR}) listed and achieved, and correct reporting units, calculational process, sample preservation, holding times)

- It notes any exceptions.
- It describes all findings in a *Verification Report*

What is Data Validation?

- Consider technical reliability and degree of confidence in reported analytical data.
- Review verification report and lab data package
  - Identify strengths and weaknesses in data
  - Obtain missing information indicated in verification report
  - Determine the presence or absence of an analyte and establish the uncertainty of the measurement process
  - Evaluate the usability of each data point by comparing data produced with MQOs and APS requirements
  - Assign data qualifiers -- possible issues that may impact meeting MQOs or APS requirements
- Validator should be a scientist with radiochemistry experience.

Data Validation

Quantitative tests and qualitative inspection for analytical detection and method uncertainty, and review of any exceptions noted from verification report

Focus moves from individual data compliance with the SOW requirements to overall project MQOs

Data Validation
(*Continued*)

- Validation will review verification exceptions ("**E**" designations) and determine if further information or qualifiers are needed
- It will apply quantitative tests to determine
  - If MQOs have been achieved
  - If analytical measurement system in good statistical control
  - If QC or Performance Test sample results meet requirements for uncertainty and method detection in the SOW/APS/QAPP
- The process assesses whether recent lab procedure changes may have affected applicability to matrix or analyte
- The validator then
  - Applies additional qualifiers to data based on tests
  - Describes all points in a *Validation Report*

Responsibility for Verification and Validation

- The Project Validation Plan is developed during project planning and is based on the SOW, APS, QAPP
  - It incorporates input from all stakeholders and
  - Must be instituted prior to initiating Data Verification and Validation
- The Project Manager assigns data verifier and data validator
  - These roles are generally be performed by different people
  - Provides for independent review and cross-checking.

Data Validation Plan
(8.3)

- The Project Data Validation Plan should contain the following information:
  - Technical and Quality Objectives (8.3.1)
    - for each sample/analyte combination, action levels and required method uncertainty (u_{MR}) (or other MQOs) and how parameters will be calculated
    - Scope of validation: percent of raw data to be reviewed; in what detail?
  - Validation criteria, specific tests and limits (8.3.2)
    - Formulas and acceptance criteria, including those for QC and PT samples, deemed appropriate to achieving project objectives.
  - Direction on qualifiers & how to assign final qualifiers (8.3.3).
  - Direction on validation report content (Section 8.3.4).

Data Verification and Validation Process
Four Stages (8.5)

Four Stages:

1. Sample handling and analysis system
2. QC sample requirements meet specified MQOs
3. Tests of detection and unusual uncertainty
4. Final data qualifiers are affixed to the individual datum

Direct evidence of the sampled material being properly analyzed is necessary:

1. Chain of custody
2. Identification
3. Preservation
4. Analysis and method
5. Sample size
6. Validity of QC samples and results
7. Analysis requirements
8. Complete reporting

QC Samples
(8.5.2)

Evidence of all QC results (indexed to the samples in a batch) should accompany the laboratory report:

- Were the types of QC samples specified in the SOW used?
- Were the correct number of QC samples per batch size used?
- Do any of the QC sample results **require** a data qualifier to be added to the sample results?

Elements Of Data Validation
(8.4)

Effective data validation must include:

- Use of an approved, pre-established data validation plan

and

- A data package that has been verified to contain the essential elements required for validation

Data Qualifier Assigned During Data Verification

E – Indicates that an exception or non-compliance has occurred. Examples of when this qualifier would be added include:

- Documentation absent from the data package
- Sample analysis radiological holding time not met
- Different procedure or unqualified analyst was used
- Calculation of concentration is not in accordance with SOW
- Several other non-compliances are possible

The "**E**" qualifier may be changed or eliminated if the particular issue can be addressed during the validation process

Qualifiers Assigned to Individual Samples During Data Validation

U: The analytical result is non-detect; the result is less than the **critical value.**

Note: the result, its uncertainty and the critical value are all reported as measured and not censored or reported as a "less than" value

Q: The reported measurement uncertainty exceeds the required method uncertainty or relative method uncertainty (φ_{MR} or u_{MR})

J: The result that is unusually uncertain or estimated

R: The result that is rejected due to severe data problems

Validation
Qualifiers Assigned to Samples Based on QC Results

S(+/-): A LCS, MS, or MSD that is above the upper control limit (+) or below the lower control limit (-)

P: A sample result with its duplicate(replicate) that exceeds a control limit

B(+/-): A blank result that is above the upper control limit (+) or below the lower control limit (-) the upper (+) or lower (-) control limit

Convention used for data validation qualifiers:

- If a sample result is above the project reporting concentration (usually the critical level)

  NO QUALIFIER IS ASSIGNED FOR DETECTION

- If all parameters associated with the sample measurement, and its associated QC samples are satisfactory

  NO QUALIFIER IS ASSIGNED

Required Method Uncertainty

Used two ways in verification and validation

- For individual data points, if the reported measurement uncertainty is greater than the required method uncertainty (u_{MR} or φ_{MR}), append data qualifier "**Q**" to the data

- In equations for QC, blanks, duplicates, and spikes to set up acceptance criteria that are statistically linked to MQOs

Detection and Unusual Uncertainty (8.5.3)

Data validator should determine if:

- The critical level has **not** been exceeded, then the "**U**" qualifier should be assigned

- The "**Q**" qualifier should be used when the reported measurement uncertainty is greater than the required method uncertainty

Data Rejection
(8.5.4)

Data rejection ("R" Qualifer) should be a rare occurrence

Three possible reasons to reject data are:

1. Insufficient or incorrect data supporting results/ documentation are available
2. Assumptions made in the planning process regarding the applicability of the method to the analysis are not true
3. High level of uncertainty ascribed to the datum

Validation Report
(8.6)

Report and narrative that summarizes the validation process and conclusions:

- List of validated sample results with cross-indexed laboratory and client identifiers
- A summary of exceptional circumstances during sample collection, receipt, storage, or analysis.
- QC sample performance and potential effect on validated data summarized in text or tabular form (including exceptional circumstances regarding validation tests)
- Summary of all validated results with associated uncertainty and final data qualifiers
- All results, uncertainty, and critical values reported “as measured”; no censored results e.g., “less than“ values

Equations Used for Validation
Matrix Spikes

- Calculate the Z statistic for each spike as follows:

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

- For matrix spike samples outside control limits,
  - Assign qualifier "S" to all samples in the associated QC batch (but not to the matrix spike itself)
  - Append a "+" sign or a "–" sign to indicate direction (above or below) of the discrepancy.
- Plot Z for each matrix spike on a control chart with warning and control limits of ±2 and ±3, respectively

Equations Used for Validation
A Matrix Spike Example

AL = 8 pCi/L; DL = 3 pCi/L; Decisions based on average

$u_{MR} = \Delta/10 = [8\text{-}3]/10 = 0.5$ pCi/L

$\varphi_{MR} = u_{MR} / UBGR = 0.5 / 8 = 0.0625$

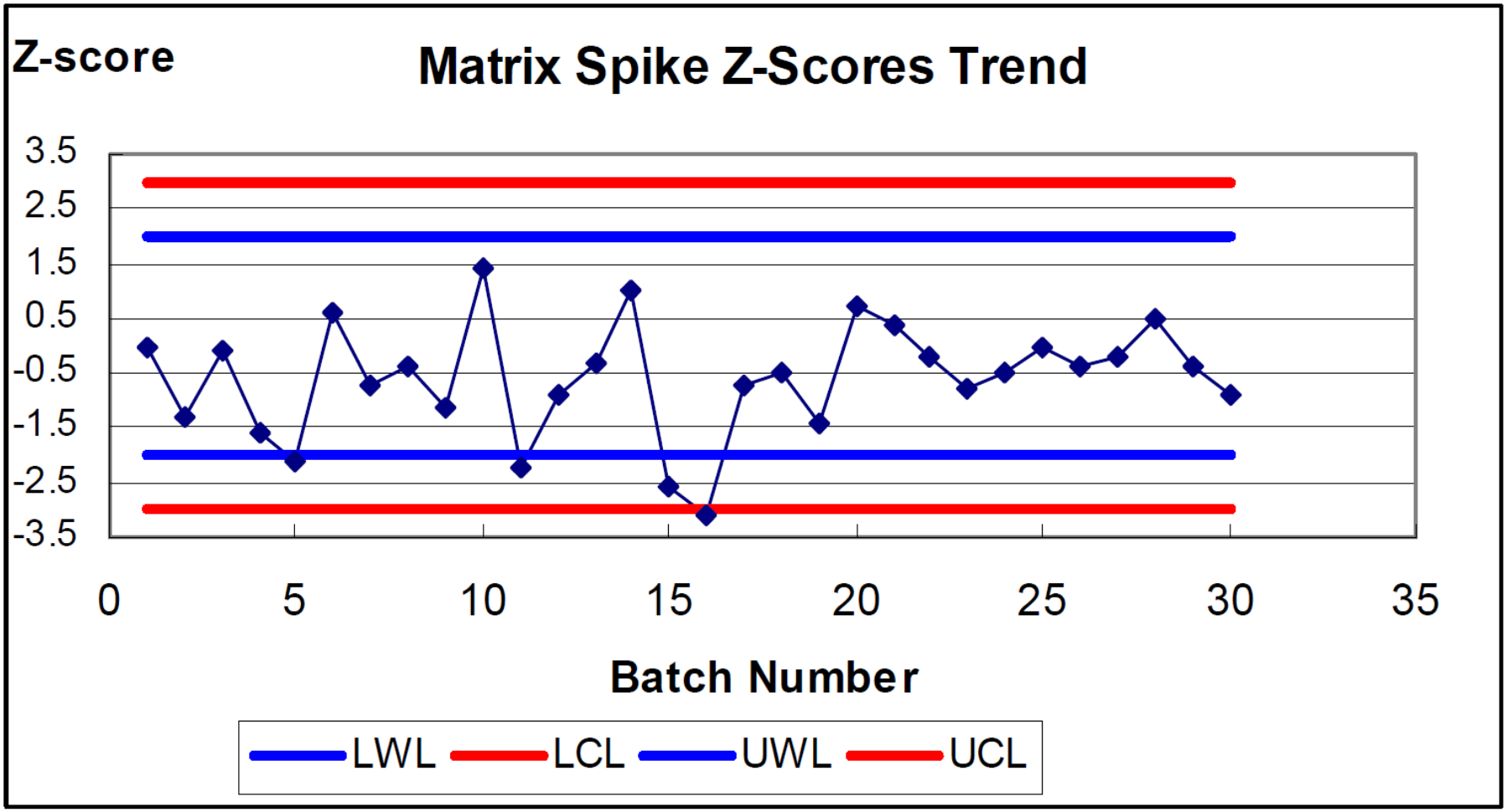
Refer to the Module 8 handout Att. B and Pages 3, 4 & 7

- We calculate Z for the ^{90}Sr matrix spike:

$$Z = \frac{15.50 - 20.0 - 1.55}{0.0625 \times \sqrt{15.50^2 + (8.0)^2}} = -5.55$$

- The matrix spike sample falls outside control limits of ±3.
  - The qualifier "S" is assigned to sample in the associated QC batch (but not to the matrix spike itself).
  - Because Z is less than -3, a "-" sign is appended to the qualifier indicating possible low bias.

Control Charting Matrix Spikes



Equations Used for Validation Duplicates

Refer to the Module 10 handout for calculations

- When $X_{avg} \leq AL$, then the warning and control limits for absolute difference are:

$$D = |x_2 - x_1| \text{ is } 2.83 \text{ and } 4.24 \times u_{MR}$$

- When $X_{avg} \geq AL$, then the warning and control limits for relative percent difference are:

$$\%D = 100\% \times 2.83 \text{ and } 4.24 \times \varphi_{MR}$$

- When a duplicate result falls outside control limits:
  - When the duplicate exceeds the limit, assign a "P" qualifier to all sample results in the associated QC batch

Equations Used for Validation
An Example with Sample Duplicates

- The mean of the two results, X_{avg}, is less than the AL of 8 pCi/L, so the control limit will be:

  2.83 & $4.24 \times u_{MR} = 1.41$ & 2.12 pCi/L

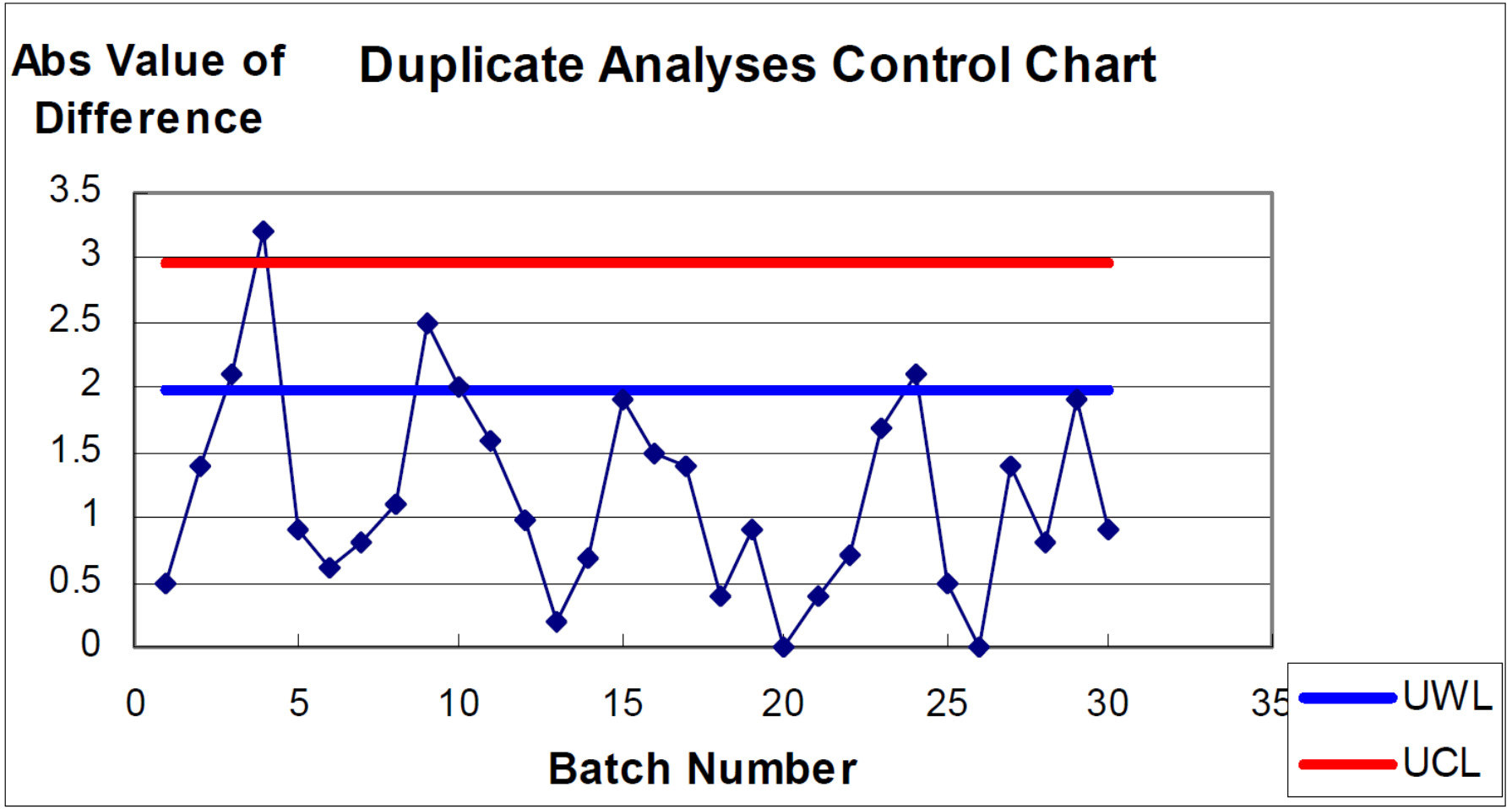
- The absolute difference of the two results is

  $|1.61 - 1.95| = 0.34$

- This is less than 2.1 pCi/L. The duplicate result is satisfactory and no qualifier is assigned.
- If X_{avg} had been 8 pCi/L or greater, the control limit would be

  RPD control limit = $100\% \times 4.24 \times \varphi_{MR} = 26.5\%$

Control Charting Duplicates – A Problem?



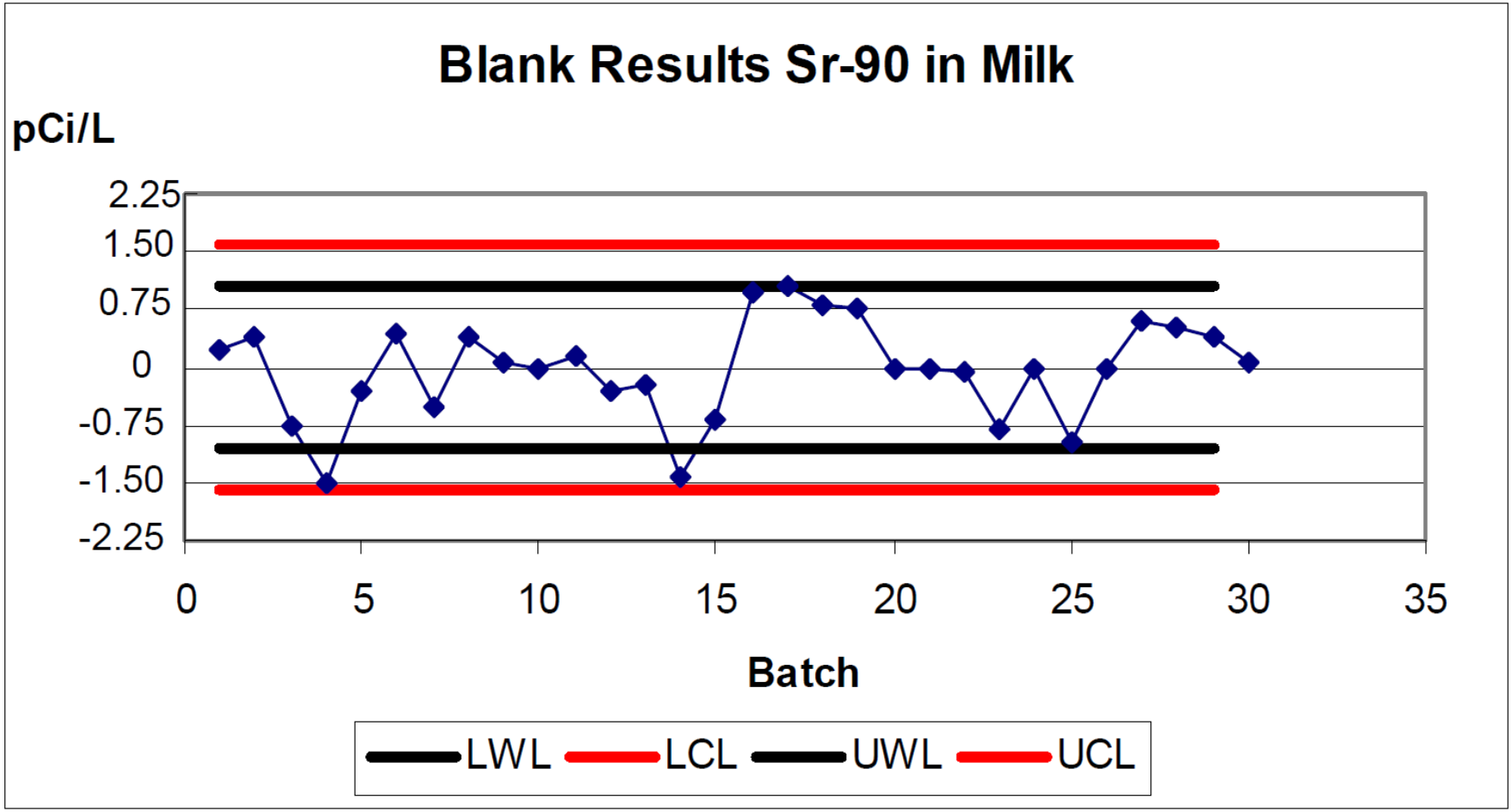
Equations Used for Validation Blanks

- Plot all blank results on a control chart with

  Warning and Control Limits = ±2 & ±3 × u_{MR}

- When a blank result falls outside the control limits:
  - Assign the "B" qualifier to the blank result to indicate that the result fell outside control limits.
  - Assign a "B" qualifier with a "+" (above) or a "–" sign (below) to all samples in the associated batch to indicate that the associated blank fell outside control limits.
- In our example, the control limits= ±3×0.5= ±1.5 pCi/L
  - The value of the blank is -0.43 pCi/L.
  - It falls within the control limits: No qualifier is necessary.

Control Charts for Blanks



Equations Used for Validation
LCS

- Calculate the %D from the data as follows:

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

- Plot %D for all LCS on a control chart with:

$$\text{Control Limits} = (\pm 3\ \varphi_{MR}) \times 100\%$$

- When an LCS result falls outside control limits:
  - Assign the qualifier "S" to all samples in the associated batch
  - Append a "+" (above) or "–" (below) sign to indicate the direction of the deviation.

Equations Used for Validation
An Example with the LCS

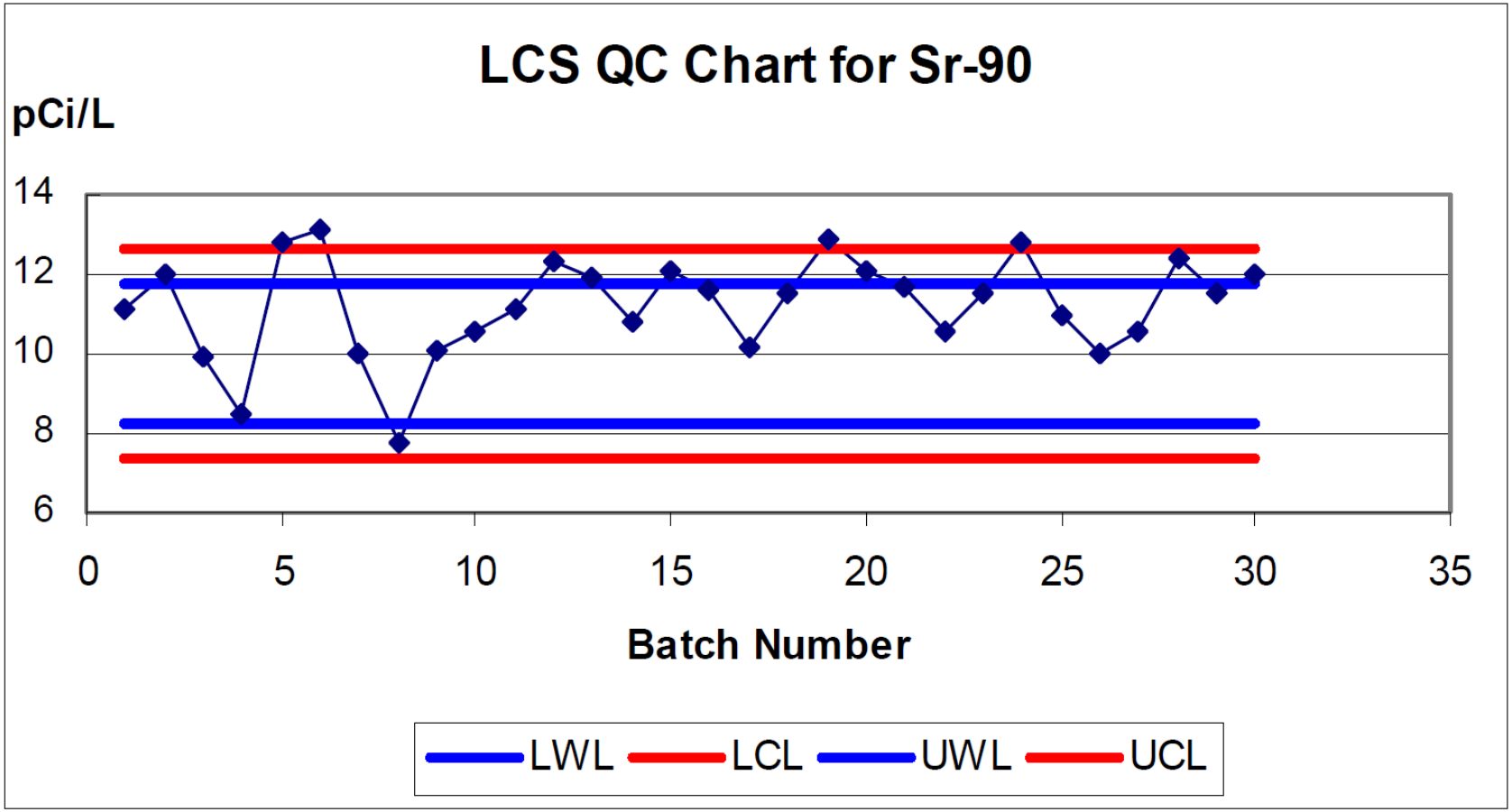
- Calculate the %D from the data as follows:

$$\%D = \frac{(SSR - SA)}{SA} \times 100\% = \frac{(12.81 - 10.0)}{10.0} \times 100\% = 28.1\%$$

- The LCS warning and control limits are

  ± 2 & $\pm 3 \times \varphi_{MR}) \times 100\%$ or 11.2% & 18.8%
- Our result clearly exceeds control limits.
- When an LCS result falls outside control limits:
  - Assign qualifier "S" to all samples in associated batch
  - Append a "+" (above) or "–" (below) sign to indicate the direction of the deviation.

Control Charts for the LCS



Finalizing Data Qualifiers

- Individual results should retain all qualifiers, although the decision making process is subject to validator judgement
  - As appropriate, assign "R" qualifiers.
  - Do "S", "P", or "B" qualifiers warrant an "R" qualifier?
  - If a tentative qualifier other than "R" assigned, or a pattern exists that warrants qualifying other results (e.g., control chart trend), assign final "S", "P", "B", "Q", or "J" qualifiers, accordingly
  - After "S", "B", or "J" are finalized consider tentative "+" and "–"
    - If potential bias is not outweighed by overall review of the data, make the + or – final
  - And finally, for "non-R" results, make tentative "U" qualifiers final
- Summarize all QC sample performance in the narrative

MARLAP Recommends …

- **MARLAP recommends the following with regard to Data Verification and Validation**

– Clearly document project objectives, implementation activities and QA/QC data in project plans

– Establish assessment criteria in the directed planning process and state them in the project plan documents

– For each analyte/sample, report the measurement result together with its expanded measurement uncertainty, sample-specific critical level, and MDC

– Qualify final measurement results with activity less than the critical level with a "**U**" for "undetected"

Final Exercise: Plutonium Fabricators

- Turn to Page 11 of the handout for the (very abbreviated) laboratory report of ^{241}Am results for the alpha spectrometry analysis of ground water samples.
- The APS specifies
  - MQO for u_{MR} is 0.98 pCi/L
  - The Action Level is 15 pCi/L
  - Batch QC will be evaluated using the default MARLAP tests we described above.
- Your mission is to evaluate and appropriately assign qualifiers to the results.

Several Key Principals to the MARLAP Process

Define the principal MQOs in any project as:

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

AND

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

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

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

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

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