General
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Running Batches, Accepting Batch Data, and Data Review

OVERVIEW

Selective and sensitive analytical methods for the quantitative evaluation of analytes in various matrixes are critical to the successful conduct of the Water Sciences Laboratory. To ensure quality data at the WSL, broad guidelines have been created to facilitate data review and reporting. These recommendations can be adjusted or modified depending on the specific type of analytical method used. Many of these parameters should be determined during method development and validation. Appropriate reporting of the laboratory data facilitates review, acceptance, and client understanding. This SOP is to serve as a general guideline for acceptance criteria and data presentation; however, the method validation report supersedes the recommendations of this SOP.

Batch acceptance criteria should be determined for each matrix, analytical group, concentration level, and analyte, if applicable. The criteria should relate to the parameters of precision, accuracy/bias, representativeness, comparability, sensitivity (quantitation limits), and completeness. The parameters indicate the qualitative and quantitative degree of quality associated with measurement data. Reporting of all necessary data and statistics aids in understanding the implications of the results. Without the appropriate accompanying information, inaccurate or incorrect conclusions may be drawn from any set of results.

LABORATORY QUALITY CHECKS INCLUDED IN BATCHES

Table 5.1: Laboratory Quality Checks

Description	Abbreviation	Definition
Laboratory Duplicate	LD	A second portion of an individual sample, treated identically to the first.
Laboratory Fortified Matrix	LFM	An additional portion of a sample to which a known concentration of the analyte(s) of interest is added.
Laboratory Fortified Blank	LFB	A reagent water or sand sample with a known concentration of the analyte(s) of interest.
Laboratory Reagent Blank	LRB	A reagent water or sand sample and all reagents, including preservatives, that are normally in contact with a sample during the entire analysis procedure.
Internal Standard	IS	A unique analyte included in each standard and added to each sample just before sample analysis.
Surrogate		A unique compound added to each sample before extraction.

BATCH ACCEPTANCE CRITERIA

Calibration Curve

A calibration curve should consist of a blank sample (matrix sample processed without internal standard), a zero sample (matrix sample processed with internal standard), and six to eight non-zero samples covering the expected range, including the Lower Limit of Quantitation (LLOQ). The simplest model that adequately describes the concentration-response relationship should be used. Selection of weighting and use of a complex regression equation should be justified. The following conditions should be met in developing a calibration curve:

- 20% deviation of the LLOQ from normal concentration
- 15% deviation of standards other than LLOQ from nominal concentration

At least four out of six non-zero standards should meet the above criteria, including the LLOQ and the calibration standard at the highest concentration. Excluding the standards should not change the model used. The correlation coefficient should be no less than 0.99, unless otherwise stated by the validation/method development report. The source, age, storage conditions, and labeling of the standards should be clearly indicated by the specific analytical method.

Quality Control Samples

Determination of Accuracy and Recovery via the Laboratory Fortified Blank (LFB):

Accuracy measurements are obtained by comparison of the results with those of a known amount of standard reference material in an appropriate matrix. The minimum requirement for ensuring accuracy is one LFB sample per twenty unknowns, or at least 5% of the total samples. Ideally, accuracy should be measured using a minimum of five determinations per concentration, and a minimum of three concentrations in the range of expected concentrations is recommended. The lowest LFB should be approximately three times the LLOQ. The mean value should be within 15% of the actual value, except at LLOQ, where it should not deviate by more than 20%.

$$PercentRecovery(\%) = \frac{X_{measured}}{X_{actual}} * 100$$

Where:

- $X_{measured}$ is the method (instrument) determined concentration for the LFB
- X_{actual} is the minimal concentration of the LFB

Determination of Selectivity via the Field Reagent Blank (FRB) and the Laboratory Reagent Blank (LFB):

For selectivity, an analysis of at least one blank sample per twenty unknown samples (at least 5% of the batch) of the appropriate matrix is necessary. Each blank sample should be tested for interference, and selectivity should be ensured if the reported value is at least half of the lower limit of quantification

(LLOQ). If the method has an IS, any determined concentration must be less than five times the signal noise of the surrounding baseline.

$$\frac{1}{2} * C_{LLOQ} > C_{blank}$$

Where:

- C_{LLOQ} is the concentration of the LLOQ
- C_{blank} is the method (instrument) determined concentration of the blank sample (5 x $X_{baseline}$ > X_{blank})
- $X_{baseline}$ is the raw data for the baseline around a peak
- X_{blank} is the raw data for the IS peak in the blank sample

Determination of Recovery via the Laboratory Fortified Matrix (LFM):

Recovery pertains to the extraction efficiency of an analytical method within the limits of variability. The recovery of an analyte is the result obtained from spiking a known amount of standard into an unknown sample and extracting it from the appropriate matrix. The result should be within 15% of the value obtained for the true concentration of the standard plus the determined value of the unknown sample. At least one LFM sample should be run per twenty unknown samples, or 5% of the batch.

$$C_{LFM} = \frac{[C_{spike} * V_{spike}] + [C_{unk} * V_{unk}]}{V_{total}}$$

Where:

- C_{LFM} is the calculated concentration of the LFM sample
- C_{spike} is the nominal concentration of the standard solution
- C_{unk} is the method determined concentration of the unknown sample
- V_{unk} is the volume of the unknown sample
- V_{spike} is the volume of the standard solution
- V_{total} is the volume of the standard solution plus the volume of the unknown sample

$$Recovery(\%) = \frac{C_{LFM}}{C_{measured}} * 100$$

Where:

- X_{LFM} is the instrument determined concentration for the LFM
- *n* is the number of replicates of the LFM
- C_{LFM} is the actual initial concentration of the LFM

Method Sensitivity via the Method Detection Limit (MDL):

The Method Detection Limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined during validation/method development; however, it should be reported with each batch, as the standard deviation of each measurement is dependent upon the MDL. The MDL should be reviewed

annually for accuracy, and the MDL cannot be greater than the lowest standard. The MDL is calculated using the following formulas:

$$StandardDeviation(S) = \sqrt{\frac{1}{n-1} * \left[\frac{\sum_{i=1}^{n} X_i^2 - \left(\sum_{i=1}^{n} X_i\right)^2}{n}\right]}$$

$$MethodDetectionLimit(MDL) = t_{99\%} * S$$

Where:

- *n* is the number of samples
- $X_{measured}$ is the method (instrument) determined concentration for the LFB
- X_{actual} is the nominal concentration of the LFB

Determination of Precision via Field Duplicates (FD1 and FD2) and Laboratory Duplicates (LD1 and LD2):

The precision of an analytical method describes the closeness of individual measures of an analyte when the procedure is applied repeatedly to multiple aliquots of a sample. At least one field and/or laboratory duplicate should be run for every twenty samples, or at least 5% of the batch. The precision determined should not exceed 15% of the coefficient of variation (CV). The coefficient of variation (CV) is determined via the following formula:

$$CV = \frac{s}{mean} * 100$$

Where:

- *s* is the method/instrument determined concentration of the sample
- The *mean* is the mean of N measurements of the same sample

DATA REVIEW REPORT

No specific template is required for the data review report, and the information provided by the instrument software, or as generated by the analyst, is generally acceptable; however, the information may need to be supplemented. Unless stated in the validation/method development report that certain information is unnecessary, the data review report should include the following information:

- **Calibration Curve**
  - Calculation model (ex. Linear, 1/x weighted linear, exponential, etc.)
  - Raw data or analyte/IS ratio for each calibration point of each analyte
  - Nominal and calculated concentration of each calibration point
  - Correlation coefficient
  - Statement of any calibration point failures
- **Quality Control Samples**
  - Raw data or analyte/IS ratio for each calibration point of each analyte
  - Nominal and calculated concentration of each calibration point
  - Dilution factor(s)

    - Percent accuracy for quality control samples, the correlation coefficient for duplicate samples, and the percent of the LLOQ for the blank samples
    - Statement of any quality control sample failures
- **Unknown Samples**
    - Raw data or analyte/IS ratio for each calibration point of each analyte
    - Method determined concentrations of each sample
    - Dilution factor(s)
- **Method Statistics**
    - The MDL for the method as determined in validation