3020

QUALITY ASSURANCE/QUALITY CONTROL

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3020 A. INTRODUCTION

Quality assurance (QA) is a laboratory operations program that specifies the measures required to produce defensible data with known precision and accuracy. This program is defined in a QA manual, written procedures, work instructions, and records. The manual must include a policy that defines the procedures to calculate statistical levels of confidence used to express data precision and bias, as well as calculation of method detection levels (MDLs) and reporting limits. The overall system includes all QA policies and quality control (QC) processes needed to demonstrate the laboratory's competence and to ensure and document the quality of its analytical data. Quality systems are essential for laboratories seeking accreditation under state or federal laboratory certification programs. Refer to Section 1020 for details on establishing a Quality Assurance Plan.

As described in Part 1000, essential QC measures may include method calibration, reagent preparation and standardization, assessment of each analyst's capabilities, analysis of blind check samples, determination of the method's sensitivity [method detection level (MDL, limit of detection (LOD), level of quantification level (LOQ), or minimum reporting level (MRL)], and daily evaluation of bias, precision, and laboratory contamination or other analytical interference.

Some methods in Part 3000 include specific QC procedures, frequencies, and acceptance criteria. These are considered the

minimum QCs needed to perform the method successfully. When the word *may* or *preferably* is used, the QC is optional but recommended; when *must* is used, the QC is required. Additional QC procedures should be used when necessary to ensure that results are valid. Some regulatory programs may require additional QC or have alternative acceptance limits. In those cases, the laboratory should follow the more stringent requirements.

The QC program consists of at least the following elements, as applicable to specific methods:

- calibration,
- continuing calibration verification (CCV),
- operational range and MDL determination,
- initial demonstration of capability (IDC),
- ongoing demonstration of capability,
- method blank or reagent blank,
- laboratory-fortified blank (LFB),
- laboratory-fortified matrix (LFM),
- duplicate sample or laboratory-fortified matrix duplicate (LFMD),
- verification of MDL and MRL,
- QC calculations,
- control charts,
- corrective action,
- frequency of QC,
- QC acceptance criteria, and
- definitions of prep and analytical batches.

Sections 1010 and 1030 describe calculations for evaluating data quality.

3020 B. Quality Control Practices

At a minimum, analysts must use the QC practices specified here unless a method specifies alternative practices. Laboratories may save time and money by purchasing premade standards, titrants, and reagents, but they still must perform the QC checks on these materials required by the analytical methods.

1. Calibration

a. Instrument calibration (not applicable to non-instrumental methods): Perform both instrument calibration and maintenance according to the manufacturer's instructions and recommendations. Conduct instrument-performance checks according to method or standard operating procedure (SOP) instructions.

b. Initial calibration: Perform initial calibration using at least 3 concentrations of standards for linear curves, at least 5 concentrations of standards for nonlinear curves, or as specified by the method. Set the lowest concentration at the reporting limit. The highest concentration standard defines the upper end of the calibration range. Ensure that the calibration range encompasses the analytical concentration values expected in samples or required dilutions.

Calibration curves may be linear through the origin, linear not through the origin, or nonlinear through or not through the origin. Some nonlinear functions can be linearized via mathematical transformations (e.g., log). The following acceptance criteria are recommended for various calibration functions. If using response factors or calibration factors, the calculated %RSD for each analyte of interest must be less than the method specified value. Refer to the method for the calibration procedure and acceptance criteria on the response or calibration factors for each analyte. If linear regression is used, use the minimum correlation coefficient specified in the method. If the minimum correlation coefficient is not specified, then a minimum value of 0.995 is recommended. Compare each calibration point to the curve by recalculating its concentration. If any recalculated concentration is not within the method's acceptance criteria, identify the source of outliers and correct before sample quantitation. Use the initial calibration with any of the above functions (response factor, calibration factor, or calibration curve) to quantitate analytes of interest in samples. Use the calibration verification (see ¶ c below) only for initial-calibration checks, not for sample quantitation, unless otherwise specified by the method. Perform initial calibration when the instrument is set up and whenever calibration-verification criteria are not met.

c. Calibration verification: In calibration verification, analysts periodically use a calibration standard to confirm that instrument performance has not changed significantly since initial calibration. Base this verification on the number of samples analyzed (e.g., after every 10 samples). Verify calibration by analyzing 1 standard at a concentration near or at the midpoint of the calibration range. Evaluate the calibration-verification analysis based either on allowable deviations from the values obtained in the initial calibration or from specific points on the calibration curve. If the calibration verification is out of control, then take corrective action, including re-analysis of any affected samples. Refer to the method for the frequency of and acceptance criteria for calibration verification. The analytical results for this second-source midrange standard must be within 10% of its true value, except for ICP-AES, which must be within 5% of its true value. If not, determine the cause of the error, take corrective action, and reverify the calibration. If the reverification passes, continue the analyses; otherwise, repeat the initial calibration.

See the individual method or manufacturer's instructions for ISE methods.

Refer to the method for CCV frequency and acceptance criteria; if not specified, use the criteria given here. Other concentrations (e.g., one near the MRL) may be used, but be aware that the acceptance criteria may vary depending on the standard's concentration.

2. Operational Range and MDL Determination

Before using a new method or instrument, determine its operational (calibration) range (upper and lower limits). Calibrate according to 3020 B.1, or verify the calibration by analyzing prepared standard solutions ranging from low to high concentrations. Determine the maximum concentration that can be measured within 10% of its true value based on the calibration curve: this is the *limit of linearity.* Dilute all samples whose concentrations are above the limit of linearity.

If reporting results <MRL, initially estimate the MDL as a concentration about 3 to 5 times lower than the minimum

calibration standard. This method for determining the MDL is based on the procedure outlined by the U.S. Environmental Protection Agency (EPA).[1]

To determine an MDL, prepare and analyze at least 7 portions of a solution spiked at or near the minimum calibration concentration and an equal number of blanks. Analysts should prepare and analyze the spikes and blanks over 3 d rather than analyzing them all in one batch. If 1 MDL will be used for multiple instruments, then the MDL analysis must be performed across all of them (however, it is unnecessary to analyze all samples on all instruments). Analysts must prepare and analyze at least 2 spikes and 2 blanks on different calendar dates for each instrument. If evaluating more than 3 instruments, then 1 set of spikes and blanks can be analyzed on multiple instruments, as long as at least 7 sets of spikes and blanks total are used. Alternatively, determine instrument-specific MDLs.

Calculate the estimated sample standard deviation, s_s, of the 7 replicates, and multiply by 3.14 to compute the MDL_s. Calculate MDL_b (MDL based on method blanks) using the following procedure.

If none of the method blanks give a numerical result (positive or negative), then MDL_b is not applicable, and MDL = MDL_s. If some give numerical results, then MDL_b equals the highest method blank result. If all of the method blanks give numerical results, calculate MDL_b as

$$MDL_b = X + 3.14S_b$$

where:

X = mean of blank results (set negative mean value to 0), and
S_b = standard deviation of blank results.

The MDL then equals whichever is greater: MDL_s or MDL_b.

If using more than 7 replicates, adjust the t value from 3.14 using student t tables with n–1 degrees of freedom.

3. Initial Demonstration of Capability

Each analyst in the laboratory should conduct an IDC at least once before analyzing any sample to demonstrate proficiency in performing the method and obtaining acceptable results for each analyte. The IDC also is used to demonstrate that a laboratory's modifications to a method will produce results as precise and accurate as those produced by the reference method. As a minimum, include a reagent blank and at least 4 LFBs at a concentration between 1 and 4 times the MRL (or other level specified in the method). Ensure that the reagent blank does not contain any analyte of interest at a concentration greater than half the lowest calibration point (or other level specified in the method). Ensure that precision and accuracy (percent recovery) calculated for LFBs are within the acceptance criteria listed in the method of choice or generated by the laboratory (if there are no established mandatory criteria).

To establish laboratory-generated accuracy and precision limits, calculate the upper and lower control limits from the mean and standard deviation of percent recovery for ≥20 data points:

$$\text{Upper control limit} = \text{Mean} + 3(\text{Standard deviation})$$
$$\text{Lower control limit} = \text{Mean} - 3(\text{Standard deviation})$$

In the absence of established mandatory criteria, use laboratory-generated acceptance criteria for the IDC or else obtain acceptance criteria from a proficiency testing (PT) provider on PT studies and translate the data to percent recovery limits per analyte and method of choice. Ensure that lab-generated criteria are at least as tight as PT-study criteria, which are typically based on either multiple lab results or PT-provider-fixed limits.

4. Ongoing Demonstration of Capability (Laboratory Control Sample)

The ongoing demonstration of capability, sometimes called a *laboratory control sample* (LCS), *laboratory control standard, QC check sample,* or *laboratory-fortified blank,* is used to ensure that the laboratory analysis remains in control while samples are analyzed and separates laboratory performance from method performance on the sample matrix. This standard should be preserved in accordance with method requirements and carried through the entire procedure, including any digestions, extraction, or filtration. Purchase an external QC standard (if available) from a reputable supplier and use the certified acceptance limits as the laboratory acceptance criteria.

Acceptance criteria vary depending on the method, matrix, and concentration. The concentration range should be either near the middle of the calibration range or near the maximum contaminant level (MCL), whichever is lower. Alternatively, prepare your own QC standard and calculate acceptance limits as ±2 standard deviations based on analysis of ≥20 replicates, unless the method specifies acceptance limits.

The ongoing demonstration of capability may be one of the following:

- acceptable performance of a blind sample analysis (single blind to the analyst);
- another IDC;
- at least 4 consecutive LCSs with acceptable levels of precision and accuracy (the laboratory shall determine acceptable precision and accuracy limits before analysis); or
- a documented analyst-review process using QC samples (QC samples can be reviewed to identify individual or group patterns and determine whether corrective action or retraining is necessary).

5. Reagent Blank

A *reagent blank* (method blank) consists of reagent water (see Section 1080) and all reagents (including preservatives) that normally are in contact with a sample during the entire analytical procedure. The reagent blank is used to determine whether and how much reagents and the preparative analytical steps contribute to measurement uncertainty. As a minimum, include 1 reagent blank with each sample set (batch) or on a 5% basis, whichever is more frequent. Analyze a blank after the CCV standard and before analyzing samples. Evaluate reagent-blank results for contamination; if contamination levels are unacceptable, identify and eliminate the source.

Positive sample results are suspect if analytes in the reagent blank are >½ MRL, unless the method specifies otherwise. Samples analyzed with a contaminated blank must be reprepared and re-analyzed unless concentrations are ≥10 times those of the blank, concentrations are nondetect, or the data user will accept

qualified data. See the method for specific reagent-blank acceptance criteria. General guidelines for qualifying sample results with regard to reagent-blank quality are as follows:

- If reagent blank is <MDL, then no qualification is required.
- If reagent blank is >½ MRL but <MRL and sample results are >MRL, then qualify results to indicate that analyte was detected in the reagent blank.
- If reagent blank is >MRL, then further corrective action and qualification is required.

6. Laboratory-Fortified Blank

A *laboratory-fortified blank* (LFB) is a reagent-water sample (with associated preservatives) to which a known concentration of the analyte(s) of interest has been added. The LFB may be used as the LCS (3020 B.4) if the method requires a preliminary sample extraction or digestion.

An LFB is used to evaluate laboratory performance and analyte recovery in a blank matrix. Its concentration should be high enough to be measured precisely, but not high enough to be irrelevant to measured environmental concentrations. The analyst should rotate LFB concentrations to cover different parts of the calibration range. As a minimum, include 1 LFB with each sample set (batch) or on a 5% basis, whichever is more frequent. (The definition of a batch is typically project-specific.)

Process the LFB through all sample preparation and analysis steps. Use an added concentration of at least 10 × MDL, or a level specified in a project plan's data quality objectives. Ideally, the LFB concentration should be less than the MCL (if the contaminant has one). Depending on method requirements, prepare the addition solution from either the same reference source used for calibration or an independent source. Evaluate the LFB for percent recovery of the added analytes by comparing results to method-specified limits, control charts, or other approved criteria. If LFB results are out of control, take corrective action, including repreparation and re-analysis of associated samples if required. Use LFB results to evaluate batch performance, calculate recovery limits, and plot control charts.

7. Laboratory-Fortified Matrix

A *laboratory-fortified matrix* (LFM) is an additional portion of a sample to which a known amount of the analytes of interest is added before sample preparation. Some analytes (e.g., speciation methods) are not appropriate for LFM analysis.

The LFM is used to evaluate analyte recovery in a sample matrix. If an LFM is feasible and the method does not specify LFM frequency requirements, then include at least 1 LFM with each sample set (batch) or on a 5% basis, whichever is more frequent. Add a concentration that is at least 10 × MRL, less than or equal to the midpoint of the calibration curve, or method-specified level to the selected samples. The analyst should use the same concentration as for LFB (3020 B.6) to allow analysts to separate the matrix's effect from laboratory performance. Prepare LFM from the same reference source used for LFB. Make the addition such that sample background levels do not adversely affect recovery (preferably adjust LFM concentrations if the known sample is more than 5 times the background level). For example, if the sample contains the analyte of interest, then add approximately as much analyte to the LFM sample as the concentration found in the known sample.

Evaluate LFM results for percent recovery; if they are not within control limits, then take corrective action to rectify the matrix effect, use another method, use the method of standard addition, or flag the data if reported. See the method for specific LFM-acceptance criteria until the laboratory develops statistically valid, laboratory-specific performance criteria. If the method does not provide limits, use the calculated preliminary limits from the IDC (3020 B.3). LFM control limits may be wider than for LFB or LCS, and batch acceptance generally is not contingent upon LFM results.

8. Duplicate Sample/Laboratory-Fortified Matrix Duplicate

Duplicate samples are analyzed to estimate precision. If an analyte is rarely detected in a matrix type, use an LFM duplicate. An *LFM duplicate* is a second portion of the sample described in 3020 B.7 to which a known amount of the analytes of interest is added before sample preparation. If sufficient sample volume is collected, this second portion of sample is added and processed in the same way as the LFM. As a minimum, include 1 duplicate sample or 1 LFM duplicate with each sample set (batch) or on a 5% basis, whichever is more frequent, and process it independently through the entire sample preparation and analysis.

Evaluate LFM duplicate results for precision and accuracy (precision alone for duplicate samples). If LFM duplicate results are out of control, then take corrective action to rectify the matrix effect, use another method, use the method of standard addition, or flag the data if reported. If duplicate results are out of control, then reprepare and re-analyze the sample and take additional corrective action, as needed. When the value of one or both duplicate samples is ≤5 × MRL, the laboratory may use the MRL as the control limit for percent recovery, and the duplicate results are not used. See method for specific acceptance criteria for LFM duplicates or duplicate samples until the laboratory develops statistically valid, laboratory-specific performance criteria. If the method does not provide limits, use the calculated preliminary limits from the IDC. In general, batch acceptance is not contingent upon LFM duplicate results.

9. Verification of MDL and MRL

With each analytical batch, analyze a reagent-water sample spiked at MRL and ensure that it meets MRL acceptance criteria (generally ±50%). If not, reanalyze the entire batch or flag results for all samples in the batch. If the MRL is biased high, nondetect (ND) samples can be reported with flags if the method or regulation allows.

If reporting to the MDL, then verify the MDL at least quarterly by analyzing a sample spiked at the same level used to determine the MDL and ensure that the result is positive. If 2 consecutive MDL-verification samples do not produce positive results, then recalculate the MDL using the most recent set of at least 7 blanks and MRL level spikes, following the protocols outlined in 3020 B.2.

10. QC Calculations

The following is a compilation of equations frequently used in QC calculations.

a. Laboratory-fortified matrix (LFM) sample (matrix spike sample):

$$\text{LFM \% Recovery} = \left[\frac{LFM\ conc \times (spike\ vol + sample\ vol) - (sample\ conc \times sample\ vol)}{spike\ solution\ conc \times spike\ vol}\right] \times 100$$

b. Relative percent difference (RPD):

$$\left[\frac{|LFM - LFMD|}{\left(\frac{LFM + LFMD}{2}\right)}\right] \times 100 = RPD$$

or

$$\left[\frac{|D_1 - D_2|}{\left(\frac{D_1 + D_2}{2}\right)}\right] \times 100 = RPD$$

where:

LFM = concentration determined for LFM,
LFMD = concentration determined for LFMD,
D1 = concentration determined for first duplicate, and
D2 = concentration determined for second duplicate.

c. Initial calibration: See Section 1020 B.12*a*.
d. Calibration verification: See Section 1020 B.12*b*.
e. Laboratory-fortified blank recovery: See Section 1020 B.12*c*.
f. Laboratory-fortified matrix: See Section 1020 B.12*e*.
g. Standard additions: See Section 1020 B.12*g*.

11. Control Charts

See Section 1020 B.13.

Reference

1. U.S. Environmental Protection Agency. III.H. Changes to method detection limit (MDL) procedure. In: Clean Water Act Methods Update Rule for the Analysis of Effluent. 40 CFR 136; 2016.

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