

## 4020 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 should include a policy that defines the statistical level of confidence used to express data precision and bias, as well as 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/or 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 4000 include specific QC procedures, frequencies, and acceptance criteria. These are considered the minimum QCs needed to perform the method successfully.

---

\* Approved by Standard Methods Committee, 2014.  
William C. Lipps (chair), Rodger B. Baird, L. Malcolm Baker, Terry E. Baxter, Andrew D. Eaton, Randy A. Gottler, John R. Gumpfer, Robin S. Parnell.

When the words *should* or *preferably* are used, the QC is recommended; when *must* is used, the QC is mandatory. 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/reagent blank,
- laboratory-fortified blank (LFB),
- laboratory-fortified matrix (LFM),
- duplicate sample/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.

## 4020 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 three concentrations of standards and one blank (for linear calibrations),

- at least five concentrations of standards and one blank (for nonlinear calibrations), or
- as many concentrations as the method specifies.

The lowest concentration must be at or below the MRL, and the highest concentration should be at the upper end of the calibration range. Make sure the calibration range encompasses the concentrations expected in method samples or required dilutions. For the most accurate results, choose calibration standard concentrations no more than one order of magnitude apart [unless calibrating pH and ion-selective electrode (ISE) methods]. Some methods and instruments respond better to more orders of magnitude between concentrations. Refer to the individual method or manufacturer's instructions for calibrating pH and ISE methods.

Apply response-factor, linear, or quadratic-curve-fitting statistics (depending on what the method allows) to analyze the concentration-instrument response relationship. If the relative

standard deviation (%RSD) of the response factors is  $\leq 15\%$ , then the average response factor may be used. Otherwise, use a regression equation. The appropriate linear or nonlinear correlation coefficient for standard concentration-to-instrument response should be  $\geq 0.995$  for linear calibrations and  $\geq 0.990$  for quadratic calibrations. Weighting factors (e.g.,  $1/x$  or  $1/x^2$ ) may be used to give more weight to the lower concentration points of the calibration. Depending on the method, calibration curves may be

- linear through the origin,
- linear not through the origin,
- nonlinear through the origin, or
- nonlinear 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 the method does not specify acceptance criteria).

Compare each calibration point to the curve and recalculate its concentration. If any recalculated values are not within the method's acceptance criteria—up to twice the MRL  $\pm 50\%$ ; between 3 and 5 times the MRL  $\pm 20\%$ ; or greater than 5 times the MRL  $\pm 10\%$ —unless otherwise specified in individual methods, identify the source of any outlier(s) and correct before sample quantitation.

NOTE: Do not use the correlation coefficient to verify a calibration's accuracy. That said, many methods still require calculation of the correlation coefficient and comparison to a specific limit.

Verify the initial calibration by analyzing a standard prepared from a different stock standard than that used to create the calibration curve; its concentration should be near the midpoint of the calibration range. The analytical results for this second-source mid-range standard must be within 10% of its true value. If not, determine the cause of the error, take corrective action, and re-verify the calibration. If the re-verification passes, continue the analyses; otherwise, repeat the initial calibration.

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

Use the initial calibration to quantitate analytes of interest in samples. Use CCV ( $\S$  c below) only for calibration checks, not for sample quantitation. Perform initial calibration when the instrument is set up and whenever CCV criteria are not met.

c. *Continuing calibration verification:* In CCV, analysts periodically use a calibration standard to confirm that instrument performance has not changed significantly since initial calibration. Base the CCV interval on the number of samples analyzed (e.g., after every 10 samples and at least once per batch). Verify calibration by analyzing one standard whose concentration is near the midpoint of the calibration range. The results must be within allowable deviations from either initial-calibration values or specific points on the calibration curve. If the CCV is out of control, then take corrective action—including re-analysis of any samples analyzed since the last acceptable CCV.

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, you should determine its operational (calibration) range (upper and lower limits). Calibrate according to 4020B.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*. All samples whose concentrations are above the limit of linearity or the highest calibration point, whichever is lower, must be diluted.

If reporting results  $< \text{MRL}$ , initially estimate the MDL as a concentration about 3 to 5 times lower than the minimum calibration standard. The method for determining the MDL is based on the procedure outlined by the U.S. Environmental Protection Agency (EPA).<sup>1</sup>

To determine an MDL, prepare and analyze at least seven 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  $\geq 3$  d rather than doing them all in one batch. If one 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 two spikes and two blanks on different calendar dates for each instrument. If evaluating more than three instruments, then one set of spikes and blanks can be analyzed on multiple instruments, so long as at least seven sets of spikes and blanks total are used. Alternatively, determine instrument-specific MDLs.

Calculate the estimated sample standard deviation,  $s_x$ , 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 values 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.

For methods in this section, spike recovery for MDL determinations must be within 50 to 150%, with a %RSD of  $< 20\%$ . If it does not meet these criteria, the MRL spiking level and calculated MDL are too low and must be repeated at a higher concentration.

## 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 four LFBs at a concentration between one and four times the MRL (or other level specified in the method). Run the IDC after analyzing all required calibration standards. 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  $\geq 20$  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

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 will 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  $\pm 2$  standard deviations based on analysis of  $\geq 20$  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 four consecutive LCSs with acceptable levels of precision and accuracy (the laboratory shall determine acceptable precision and accuracy limits before analysis and shall tabulate or be able to readily retrieve four consecutive passing LCSs per method per analyst per year); 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).

If none of these options is technically feasible, then review the analyses of real-world samples to ensure that results are within predefined acceptance criteria (established by the laboratory or method, whichever is tighter).

#### 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 one 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 analyte(s) in the reagent blank are  $> 1/2\text{MRL}$ , unless the method specifies otherwise. Samples analyzed with a contaminated blank must be re-prepared and re-analyzed unless concentrations are  $\geq 10$  times those of the blank, concentrations are nondetect, or data user will accept qualified data. See 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  $< \text{MDL}$  and sample results are  $> \text{MRL}$ , then no qualification is required.
- If reagent blank is  $> 1/2\text{MRL}$  but  $< \text{MRL}$  and sample results are  $> \text{MRL}$ , then qualify results to indicate that analyte was detected in the reagent blank.
- If reagent blank is  $> \text{MRL}$ , 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 (4020B.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 one 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  $10 \times \text{MDL}$ , at or below the midpoint of the calibration curve, a method-specified level, 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

QUALITY ASSURANCE/QUALITY CONTROL (4020)/Quality Control Practices

TABLE 4020:I. MINIMUM QUALITY CONTROLS FOR METHODS IN PART 4000

SECTION	METHOD BLANK	LFB*	LFM† & LFMD‡	OTHER	SECTION	METHOD BLANK	LFB*	LFM† & LFMD‡	OTHER
4110B	×	×	×	1,3	4500-N B	×	×	×	3
4110C	×	×	×	1,3	4500-N C	×	×	×	3
4110D	×	×	×	1,3	4500-N D	×	×	×	3
4120B	×	×	×	1,3	4500-NH <sub>3</sub> C	×	×	×	7
4140	×	×	×	1,3	4500-NH <sub>3</sub> D	×	×	×	9
					4500-NH <sub>3</sub> E	×	×	×	9
4500-B.B	×	×	×	3	4500-NH <sub>3</sub> F	×	×	×	3
4500-B.C	×	×	×	3	4500-NH <sub>3</sub> G	×	×	×	3
					4500-NH <sub>3</sub> H	×	×	×	3
4500-Br <sup>-</sup> B	×	×	×	3	4500-NO <sub>2</sub> <sup>-</sup> B	×	×	×	3
4500-Br <sup>-</sup> D	×	×	×	3					
					4500-NO <sub>3</sub> <sup>-</sup> B	×	×	×	3
4500-CO <sub>2</sub> B	-	-	-	4	4500-NO <sub>3</sub> <sup>-</sup> C	×	×	×	3
4500-CO <sub>2</sub> C	×	-	-	2,8	4500-NO <sub>3</sub> <sup>-</sup> D	×	×	×	9
4500-CO <sub>2</sub> D	×	-	-	2	4500-NO <sub>3</sub> <sup>-</sup> E	×	×	×	3
					4500-NO <sub>3</sub> <sup>-</sup> F	×	×	×	3
4500-CN <sup>-</sup> C	×	×	×	3	4500-NO <sub>3</sub> <sup>-</sup> H	×	×	×	3
4500-CN <sup>-</sup> D	×	×	×	8	4500-NO <sub>3</sub> <sup>-</sup> I	×	×	×	3
4500-CN <sup>-</sup> E	×	×	×	3					
4500-CN <sup>-</sup> F	×	×	×	9	4500-N <sub>org</sub> B	×	×	×	3
4500-CN <sup>-</sup> G	×	×	×	3	4500-N <sub>org</sub> C	×	×	×	3
4500-CN <sup>-</sup> H	×	×	×	3	4500-N <sub>org</sub> D	×	×	×	3
4500-CN <sup>-</sup> I	×	×	×	3					
4500-CN <sup>-</sup> J	×	-	-	3	4500-O B	-	-	-	2,7
4500-CN <sup>-</sup> L	×	×	×	9	4500-O C	-	-	-	2,7
4500-CN <sup>-</sup> M	×	×	×	3	4500-O E	-	-	-	2,7
4500-CN <sup>-</sup> N	×	×	×	3	4500-O F	-	-	-	2,7
4500-CN <sup>-</sup> O	×	×	×	3	4500-O G	-	-	-	2,6
					4500-O H				2,6
4500-Cl B	×	×	-	2,7					
4500-Cl C	×	×	-	2,7	4500-O <sub>3</sub> B	×	-	-	2
4500-Cl D	×	×	-	2,7					
4500-Cl E	×		-	2,7	4500-P C	×	×	×	3
4500-Cl F	×	×	-	2,7	4500-P D	×	×	×	3
4500-Cl G	×	×	-	2,3	4500-P E	×	×	×	3
4500-Cl H	×	×	-	2,3	4500-P F	×	×	×	3
4500-Cl I	×	×	-	2,9	4500-P G	×	×	×	3
					4500-P H	×	×	×	3
4500-Cl <sup>-</sup> B	×	×	×	7	4500-P I	×	×	×	3
4500-Cl <sup>-</sup> C	×	×	×	7	4500-P J	×	×	×	3
4500-Cl <sup>-</sup> D	×	×	×	7					
4500-Cl <sup>-</sup> E	×	×	×	3	4500- KMnO <sub>4</sub> B	×	×	×	3
4500-Cl <sup>-</sup> G	×	×	×	3					
					4500-SiO <sub>2</sub> C	×	×	×	3
4500-ClO <sub>2</sub> B	×	-	-	7	4500-SiO <sub>2</sub> D	×	×	×	3
4500-ClO <sub>2</sub> C	×	-	-	7	4500-SiO <sub>2</sub> E	×	×	×	3
4500-ClO <sub>2</sub> E	×	-	-	7	4500-SiO <sub>2</sub> F	×	×	×	3
4500-F <sup>-</sup> C	×	×	×	9	4500-S <sup>2-</sup> D	×	×	×	3
4500-F <sup>-</sup> D	×	×	×	3	4500-S <sup>2-</sup> E	×	×	×	3
4500-F <sup>-</sup> E	×	×	×	3	4500-S <sup>2-</sup> F	×	×	×	7
4500-F <sup>-</sup> G	×	×	×	3	4500-S <sup>2-</sup> G	×	×	×	9
					4500-S <sup>2-</sup> I	×	×	×	3
4500-H <sup>+</sup> B	-	-	-	2,5,9	4500-S <sup>2-</sup> J	×	×	×	3
4500-I B	×	×	×	3	4500-SO <sub>3</sub> <sup>2-</sup> B	×	×	-	7
4500-I C	×	×	×	7	4500-SO <sub>3</sub> <sup>2-</sup> C	×	×	-	3

TABLE 4020:I. CONT.

SECTION	METHOD BLANK	LFB*	LFM† & LFMD‡	OTHER	SECTION	METHOD BLANK	LFB*	LFM† & LFMD‡	OTHER
4500-I <sup>-</sup> B	×	×	×	3	4500-SO <sub>4</sub> <sup>2-</sup> C	×	×	×	8
4500-I <sup>-</sup> C	×	×	×	3	4500-SO <sub>4</sub> <sup>2-</sup> D	×	×	×	8
4500-I <sup>-</sup> D	×	×	×	7	4500-SO <sub>4</sub> <sup>2-</sup> E	×	×	×	3
					4500-SO <sub>4</sub> <sup>2-</sup> F	×	×	×	3
4500-IO <sub>3</sub> <sup>-</sup> B	×	×	×	7	4500-SO <sub>4</sub> <sup>2-</sup> G	×	×	×	3

\* Laboratory-fortified blank.

† Laboratory-fortified matrix.

‡ Laboratory-fortified matrix duplicate.

× indicates that a QC type is mandatory for the method.

1. Additional QC guidelines in method.

2. Duplicates of the sample will be run.

3. Refer to 4020B for further QC requirements.

4. Compare to results from Section 4500-CO<sub>2</sub>D.

5. Additional QC check with pH standard whose value is bracketed by calibration standards.

6. Zero check with zero oxygen sample.

7. Refer to 4020B for other QC requirements, no calibration curve required (use or standardize against a primary standard).

8. Refer to 4020B for other QC requirements, no calibration curve required (verify the accuracy of analytical balances with NIST-traceable weights).

9. Refer to 4020B for other QC requirements (verify slope according to manufacturer's instructions).

This table is not comprehensive; refer to the specific method and 4020B for further details.

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 re-preparation 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 analyte(s) of interest is added before sample preparation. Some analytes are not appropriate for LFM analysis; see Table 4020:I and specific methods for guidance on when an LFM is relevant.

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 one 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 sample(s). The analyst should use the same concentration as for LFB (4020B.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 five times the background level). At a minimum, the spike must at least equal the background concentration, unless the method specifies otherwise. 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 method for specific LFM-acceptance criteria until the laboratory develops statisti-

cally valid, laboratory-specific performance criteria. If the method does not provide limits, use the calculated preliminary limits from the IDC (4020B.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 4020B.7 to which a known amount of the analyte(s) 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 one duplicate sample or one 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 re-prepare 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 to measure precision. 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  $\pm 50\%$ ). If not, re-analyze 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 two 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 4020B.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):*

LFM % Recovery =

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

*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,

*D*<sub>1</sub> = concentration determined for first duplicate, and

*D*<sub>2</sub> = concentration determined for second duplicate.

*c. Initial calibration:* See Section 1020B.12a.

*d. Calibration verification:* See Section 1020B.12b.

*e. Laboratory-fortified blank recovery:* See Section 1020B.12c.

*f. Laboratory-fortified matrix:* See Section 1020B.12e.

*g. Standard additions:* See Section 1020B.12g.

## 11. Control Charts

See Section 1020B.13.

## 12. Reference

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 2016. III.H. Changes to method detection limit (MDL) procedure. *In* Clean Water Act Methods Update Rule for the Analysis of Effluent. 40 CFR 136.