5020 QUALITY ASSURANCE/QUALITY CONTROL*

5020 A. Introduction

Without quality control (QC), there is no confidence in sample results. As described in Part 1000, essential QC measures include calibration, reagent standardization, assessment of each analyst's demonstration of capabilities, analysis of blind check samples, determination of the method's sensitivity [method detection level (MDL) or minimum reporting level (MRL)], and regular evaluation of bias, precision, and the presence of laboratory contamination or other analytical interference. The details of these procedures, their performance frequency, and expected ranges of results should be formalized in a written Quality Assurance Manual and standard operating procedures.

Some of the methods in Part 5000 include specific QC procedures, frequencies, and acceptance criteria. These are considered to be the minimum quality controls needed to perform the method successfully. Additional QC procedures can and should be used. Some regulatory programs may require additional QC or have alternative acceptance limits.

Each method typically includes acceptance-criteria guidance for precision and bias of test results. If not, the laboratory should determine its own criteria (e.g., using control-charting techniques). For some Part 5000 procedures (e.g., the BOD procedure) the traditional determination of accuracy—adding a known amount of analyte to either a sample or a blank—is not practical. This does not, however, relieve analysts of the responsibility for evaluating test accuracy. Instead, obtain certified ready-made analytes for such tests.

Evaluate precision by analyzing duplicate or spiked duplicate samples.

To help verify the accuracy of calibration standards and overall method performance, participate in an annual or preferably more frequent program of analysis of single-blind QC check samples (QCS)—ideally provided by an external entity. Such programs are sometimes called *proficiency testing (PT)/performance evaluation (PE) studies*. An unacceptable result on a PT sample is often a strong indication that a test protocol is not being followed successfully. Investigate circumstances fully to find the cause. In many jurisdictions, participation in PT studies is a required part of laboratory certification/accreditation.

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5020 B. Quality Control Practices

1. Initial Quality Control

a. Initial demonstration of capability (IDC): Before analysts run any samples, verify their capability with the method. Run a laboratory-fortified blank (LFB) (5020B.2*e*) at least four times and compare to the limits listed in the method. If no limit is specified, use the following procedure to establish limits:

Calculate the standard deviation of the four samples. The LFB's recovery limits are

$$\text{LFB's initial recovery limits} = \text{Mean} \pm (5.84 \times \text{Standard Deviation})$$

where

5.84 = the two-sided Student's *t* factor for 99% confidence limit for three degrees of freedom.[1]

Also, verify that the method is sensitive enough to meet measurement objectives for detection and quantitation by determining the lower limit of the operational range. (For basic guidance on demonstrating capability, see Section 1020B.)

b. Method detection level (MDL): If data will be reported below the calibrated range, then before analyzing samples, determine the MDL for each analyte via Section 1020 or other applicable procedures.[2] MDL determination is not required if 1) data are not reported below the instrument's calibrated range, and 2) the ability to provide quantitative data at the reporting limit is verified. If MDL is determined, verify MDL at least annually for each analyte in a method and major matrix category. The laboratory should define all matrix categories in its QA plan. Review MDL requirements as per Section 1020. Analyze samples for MDL determinations over at least a 3-d period to generate a realistic value. Include all sample-preparation steps in the MDL determination. Using data from the low-level LFBs included in each analytical run is an economical way to calculate MDL.

Ideally, use pooled data from several analysts rather than data from one analyst. (For specific information on MDLs and pooling data, see Section 1020B.) To verify the MDL annually on each instrument used in the laboratory, analyze a QC sample (subjected to all sample-preparation steps) spiked at a level 1 to 4 times the MDL. A successful verification is one that meets all the method's detection criteria.

c. Operational range: Before using a new method or instrument, determine its operational range (upper and lower limits) or at least verify that the intended range of use is within the operational range. For each analyte, use standard concentrations that provide increasing instrument response. The MRL is set to a concentration at or above the lowest standard used in the analysis. Verify quantitation at the MRL initially and at least quarterly (preferably daily) by analyzing a QC sample (subjected to all sample-preparation steps) spiked at a level 1 to 2 times the

MRL. A successful verification meets the method's or laboratory's accuracy requirements at the MRL. Laboratories must define acceptance criteria for the operational range, including the MRL, in their QA documentation.

2. Ongoing Quality Control

a. Calibration: Calibrate the method using the directions in the procedure. Appropriate calibrations may be linear, weighted or second order. (For basic calibration guidance, see Section 1020B.)

b. Calibration verification: Verify calibration by periodically analyzing a calibration standard and calibration blank during a run—typically, after each batch of ten samples and at the end of the run. The analyte concentration in calibration-verification standards should be varied over the calibration range to determine detector response.

For the calibration verification to be valid, (unless the method specifies otherwise) check standard results must not exceed ±10% of its true value, and calibration blank results must not be greater than one-half the reporting level.

If a calibration verification fails, immediately cease analyzing samples and initiate corrective action. Then, re-analyze the calibration standard and blank. If the calibration verification passes, continue the analysis. Otherwise, repeat initial calibration and re-analyze samples run since the last acceptable calibration verification.

If the LFB is not prepared from a second source to confirm method accuracy, (unless the method specifies otherwise) the laboratory must also verify the accuracy of its standard preparation by analyzing a mid-level second-source calibration standard whenever a new initial calibration curve is prepared. Results must agree within 15% unless otherwise specified in a method.

c. Quality control sample (QCS): Analyze an externally generated, blind QCS (unknown concentration) at least annually (preferably semi-annually or quarterly). Obtain this sample from a source external to the laboratory, and compare results to that source's acceptance results. If testing results do not pass acceptance criteria, investigate why, take corrective action, and analyze a new QCS. Repeat this process until results meet the acceptance criteria.

d. Method blank (MB): When appropriate (Table 5020:I), include at least one MB daily or with each batch of 20 or fewer samples, whichever is more frequent. Any constituent(s) recovered must generally be less than or equal to one-half the reporting level (unless the method specifies otherwise). If any MB measurements are at or above the reporting level, take immediate corrective action as outlined in Section 1020B. This may include re-analyzing the sample batch or qualifying the reported data. Sample results less than MRL are considered valid even if the MB has a positive result, but should be flagged.

e. Laboratory-fortified blank (LFB): Section 1020 currently specifies that LFBs and LFMs be made from a second source. However, as long as each initial calibration solution is verified via a second source (5020B.2*b*), the LFB/LFM need not be from a second source (unless the method specifies otherwise).

Using stock solutions (preferably prepared with a second source), prepare fortified concentrations so they are within the calibration curve. Ideally, vary LFB concentrations to cover the range from the midpoint to the lower part of calibration curve, including the reporting limit.

TABLE 5020:I. MINIMUM QUALITY CONTROL FOR METHODS IN PART 5000

Section	Analyte	Method Blank	LFB*	LFM† & LFMD‡	Other
5210B	BOD	-	-	-	1,2,3
5210C		-	-	-	1,2,3
5210D		-	-	-	1,2,3
5220B	COD	×	×	×	1,2,3
5220C		×	×	×	1,2,3
5220D		×	×	×	1,2,3
5310B	TOC	×	×	×	1,2,3
5310C		×	×	×	1,2,3
5310D		×	×	×	1,2,3
5320B	Dissolved Organic Halogen	×	×	×	1,2,3
5510B	Aquatic Humic Substances	×	×	×	1,2,3
5510C		×	×	×	1,2,3
5520B	Oil and Grease	×	×	×	1,2,3
5520C		×	×	×	1,2,3
5520D		×	×	×	1,2,3
5520E		×	×	×	1,2,3
5520F		×	×	×	1,2,3
5520G		×	×	×	1,2,3
5530B§	Phenols	×	×	×	1,2,3
5530C		×	×	×	1,2,3
5530D		×	×	×	1,2,3
5540B§	Surfactants	×	×	×	1,2,3
5540C		×	×	×	1,2,3
5540D		×	×	×	1,2,3
5550B	Tannin and Lignin	×	×	×	1,2,3
5560B§	Organic/Volatile Acids	×	×	×	1,2,3
5560C§		×	×	×	1,2,3
5560 D		×	×	×	1,2,3
5710B	THMs and DBPs	-	-	-	1,2,3
5710C		-	-	-	1,2,3
5710D		-	-	-	1,2,3
5910B	UV-Absorbing Organic Constituents	×	-	-	1,2,3

* Laboratory-fortified blank.
† Laboratory-fortified matrix.
‡ Laboratory-fortified matrix duplicate.
§ A sample preparation technique that is normally combined with a subsequent determinative technique
× indicates that a QC type is mandatory for the method.
- indicates that a QC type is not mandatory for the method.
1. Additional QC guidelines in method.
2. Duplicates or LFMD of the sample will be run.
3. Refer to 5020B for further QC requirements.
This table is not comprehensive; refer to the specific method and 5020B for further details.

Calculate percent recovery, plot control charts, and determine control limits (Section 1020B) for these measurements. Use the control limits to determine ongoing demonstration of capability

limits. Some methods may have specific limits to use in lieu of plotting control charts; if so, control charts may still be useful in identifying potential problems. Ensure that the LFB meets the method's performance criteria when such criteria are specified. Establish corrective actions to be taken if the LFB does not satisfy acceptance criteria.

When appropriate (Table 5020:I), include at least one LFB daily or per each batch of 20 or fewer samples. Some regulatory programs require a higher frequency of LFBs.

f. Duplicates: When appropriate (Table 5020:I), randomly select routine samples to be analyzed twice. Process duplicate sample independently through the entire sample preparation and analysis procedure. Include at least one duplicate for each matrix type daily or with each batch of 20 or fewer samples. (Some regulatory programs require more frequent use of duplicates.) Calculate control limits for duplicates when method-specific limits are not provided. When appropriate (Table 5020:I), run either a sample duplicate or an LFMD per batch. It is not necessary to perform both. (For basic guidance on duplicates, see Section 1020B.)

g. Laboratory-fortified matrix (LFM)/Laboratory-fortified matrix duplicate (LFMD): When appropriate for the analyte (Table 5020:I), include at least one LFM/LFMD daily or with each batch of 20 or fewer samples. (Some regulatory programs require more frequent use of LFMs. For basic guidance on LFMs and LFMDs, see Section 1020B.)

To prepare an LFM, add a known concentration of analytes (ideally from a second source) to a randomly selected routine sample without increasing its volume by more than 5%. Ideally, the new concentration should be at or below the midpoint of the calibration curve, and for maximum accuracy, the spike should approximately double the sample's original concentration. If necessary, dilute the spiked sample to bring the measurement within the calibration curve. Also, rotate the range of spike concentrations to verify performance at various levels.

Calculate percent recovery and relative percent difference, plot control charts (unless the method specifies acceptance criteria), and determine control limits for spikes at different concentrations (Section 1020B). Ensure that the method's performance criteria are satisfied.

Process fortified samples independently through entire sample preparation and analysis procedure.

3. Calculations

a. LFM recovery:

$$\frac{(C_s \times f) - C}{S} \times 100 = \%\ \text{Recovery LFM or LFMD}$$

where:

C_s = LFM concentration determined experimentally,
f = spike dilution correction,
C = concentration of sample before spiking, and
S = concentration of spike.

Note: f should be more than 0.95. Spiking that dilutes a sample by more than 5% changes the matrix significantly. Ideally, keep f above 0.99 (equivalent to 1% dilution of sample due to spike addition) so f can be ignored and the equation simplified to eliminate f.

b. LFB recovery:

$$\frac{C_b}{I} \times 100 = \%\ \text{Recovery LFB}$$

where:

C_b = LFB concentration determined experimentally, and
I = initial concentration of analytes added to LFB.

c. Relative percent difference:

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

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_1 = concentration determined for first duplicate, and
D_2 = concentration determined for second duplicate.

4. References

1. Meier, P.C. & E.E. Zünd. 2000. Statistical Methods in Analytical Chemistry, 2nd ed. Wiley Interscience, New York, N.Y.
2. U.S. Environmental Protection Agency. 1995. Definition and procedure for the determination of the method detection limit, rev. 1.11, 40 *CFR* Part 136, Appendix B. *Fed. Reg.* 5:23703.