4020 QUALITY ASSURANCE/QUALITY CONTROL*

4020 A. Introduction

Without both quality-control (QC) and sample results, there is no confidence in the results of analytical tests. As described in Part 1000, essential QC measures include method calibration, reagent standardization, assessment of each analyst's capabilities, analysis of blind check samples, determination of the method's sensitivity (method detection level or quantification limit), and daily 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 4000 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 via control-charting techniques. For some Part 4000 procedures, including pH, dissolved oxygen, residual chlorine, and carbon dioxide, the traditional determination of bias—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 bias. Instead, obtain certified ready-made analyte solutions for such tests.

Evaluate precision by analyzing duplicate samples.

To help verify the accuracy of calibration standards and overall method performance, participate in an annual or preferably semi-annual 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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4020 B. Quality Control Practices

1. Initial Quality Control

a. Initial demonstration of capability (IDC): Before new analysts run any samples, verify their capability with the method. Run a laboratory-fortified blank (LFB) (4020B.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 limits and 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): Before analyzing samples, determine the MDL for each analyte via Section 1020B.4, 1030C, or other applicable procedures.[2] Verify MDL at least annually for each analyte in a method and matrix category. The laboratory should define all matrix categories in its QA plan. Review MDL requirements as per Sections 1020B.4 and 1030C. 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.

Ideally, use pooled data from several analysts rather than data from one analyst. (For specific information on MDLs and pooling, see Sections 1020B.4 and 1030C.)

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 minimum reporting level (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 initially with at least one blank and three calibration standards of the analyte(s) of interest. If using

second-order fits, include at least five standards and one blank. Depending on methods, the appropriate calibrations may be linear, weighted linear, or second order.

Select calibration standards that bracket the sample's expected concentration and are within the method's operational range. The number of calibration points depends on the width of the operational range and the shape of the calibration curve. One calibration standard should be at or below the method's reporting limit.

As a general rule, differences among calibration standard concentrations should not be greater than one order of magnitude (i.e., 1, 10, 100, 1000). However, most methods for inorganic nonmetals do not have wide operational ranges, so the concentrations in their initial calibration standards should be less than one order of magnitude apart. For example, concentration variables of 1, 5, 10, and 50 can be used if the operational range is less than two orders of magnitude.

Apply linear or polynomial curve-fitting statistics, as appropriate, to analyze the concentration–instrument response relationship. The appropriate linear or nonlinear correlation coefficient for standard concentration-to-instrument response should be greater than or equal to 0.995. Back calculate the concentration of each calibration point. The back-calculated and true concentrations should agree within ±10%, unless different criteria are specified in an individual method. At the lower limit of the operational range, acceptance criteria are usually wider. Such criteria must be defined in the laboratory's QA plan.

Use initial calibration to quantify analyte concentrations in samples. Use calibration verification only to check the initial calibration, not to quantify samples. Repeat initial calibration daily or when starting a new batch of samples, unless the method permits calibration verification between batches. (For basic calibration guidance, see Section 1020B.11)

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 calibration verification standard's analyte concentration should be varied over the calibration range to determine detector response.

For the calibration verification to be valid, 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 (unless the method specifies otherwise).

If a calibration verification fails, immediately cease analyzing samples and initiate corrective action. Then, re-analyze the calibration verification. 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, 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 laboratory'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): 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.5. This may include re-analyzing the sample batch.

e. Laboratory-fortified blank (LFB): LFBs and LFMs do not have to be made from a second source (unless the method specifies otherwise) as long as each initial calibration solution is verified via a second source (4020B.2*b*).

Using stock solutions (preferably prepared with the 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.

Calculate percent recovery, plot control charts, and determine control limits (Section 1020B.13) for these measurements. Use the control limits to determine ongoing demonstration of capability (ODC). 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.

Include at least one LFB daily or per each batch of 20 or fewer samples. Some regulatory programs require a higher frequency of LFBs. If the sample results are often "nondetect," consider using duplicate LFBs to assess precision.

f. Duplicates: When appropriate (Table 4020:I), randomly select routine samples to be analyzed twice. Process duplicate sample independently through the entire sample preparation and analysis. Include at least one duplicate for each matrix type daily or with each batch of 20 or fewer samples. Calculate control limits for duplicates when method-specific limits are not provided. (For basic guidance on duplicates, see Section 1020B) Some regulatory programs require more frequent use of duplicates.

g. Laboratory-fortified matrix (LFM)/Laboratory-fortified matrix duplicate (LFMD): When appropriate for the analyte (Table 4020:I), include at least one LFM/LFMD daily or with each batch of 20 or fewer samples. (For basic guidance on LFMs and LFMDs, see Section 1020B.7 and 8). Some regulatory programs require more frequent use of LFMs.

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 con-

centrations (Section 1020B.13). Ensure that the method's performance criteria are satisfied.

Process fortified samples independently through entire sample preparation and analysis.

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 greater than 0.95. More than 5% dilution due to spiking changes the matrix significantly. Ideally, keep f to above 0.99 (equivalent to 1% dilution of sample due to spike addition), in which case 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.

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

Section	Method Blank	LFB*	LFM† & LFMD‡	Other
4110B	×	×	×	1,3
4110C	×	×	×	1,3
4110D	×	×	×	1,3
4140	×	×	×	1,3
4500-B.B	×	×	×	3
4500-B.C	×	×	×	3
	×			
4500-Br^- B	×	×	×	3
4500-Br^- D	×	×	×	3
4500-CO_2 B	–	–	–	4
4500-CO_2 C	×	–	–	2
4500-CO_2 D	×	–	–	2
4500-CN^- C	×	×	×	3
4500-CN^- D	×	×	×	3
4500-CN^- E	×	×	×	3
4500-CN^- F	×	×	×	3
4500-CN^- G	×	×	×	3
4500-CN^- H	×	×	×	3
4500-CN^- I	×	×	×	3
4500-CN^- J	×	×	×	3
4500-CN^- L	×	×	×	3
4500-CN^- M	×	×	×	3
4500-CN^- N	×	×	×	3
4500-CN^- O	×	×	×	3

Section	Method Blank	LFB*	LFM† & LFMD‡	Other
4500-Cl B	×	×	–	2,3
4500-Cl C	×	×	–	2,3
4500-Cl D	×	×	–	2,3
4500-Cl F	×	×	–	2,3
4500-Cl G	×	×	–	2,3
4500-Cl H	×	×	–	2,3
4500-Cl I	×	×	–	2,3
4500-Cl^- B	×	×	×	3
4500-Cl^- C	×	×	×	3
4500-Cl^- D	×	×	×	3
4500-Cl^- E	×	×	×	3
4500-Cl^- G	×	×	×	3
4500-ClO_2 C	×	×	×	3
4500-ClO_2 E	×	×	×	3
4500-F^- C	×	×	×	3
4500-F^- D	×	×	×	3
4500-F^- E	×	×	×	3
4500-F^- G	×	×	×	3
4500-H^+ B	–	–	–	2,5
4500-I B	×	×	×	3
4500-I C	×	×	×	3
4500-I^- B	×	×	×	3
4500-I^- C	×	×	×	3
4500-I^- D	×	×	×	3

TABLE 4020:I. CONT

Section	Method Blank	LFB*	LFM† & LFMD‡	Other
4500-IO_3^- B	×	×	×	3
4500-N B	×	×	×	3
4500-N C	×	×	×	3
4500-N D	×	×	×	3
4500-NH_3 C	×	×	×	3
4500-NH_3 D	×	×	×	3
4500-NH_3 E	×	×	×	3
4500-NH_3 F	×	×	×	3
4500-NH_3 G	×	×	×	3
4500-NH_3 H	×	×	×	3
4500-NO_2^- B	×	×	×	3
4500-NO_3^- B	–	–	–	3
4500-NO_3^- C	×	×	×	3
4500-NO_3^- D	×	×	×	3
4500-NO_3^- E	×	×	×	3
4500-NO_3^- F	×	×	×	3
4500-NO_3^- H	×	×	×	3
4500-NO_3^- I	×	×	×	3
4500-N_{org} B	×	×	×	3
4500-N_{org} C	×	×	×	3
4500-N_{org} D	×	×	×	3
4500-O C	–	–	–	2,6
4500-O E	–	–	–	2,6
4500-O F	–	–	–	2,6
4500-O_3 B	×	–	–	2
4500-O G	–	–	–	2,6
4500-O B	–	–	–	2,6
4500-P C	×	×	×	3
4500-P D	×	×	×	3
4500-P E	×	×	×	3
4500-P F	×	×	×	3
4500-P G	×	×	×	3
4500-P H	×	×	×	3
4500-P I	×	×	×	3
4500-P J	×	×	×	3
4500-$KMnO_4$ B	×	×	×	3
4500-SiO_2 C	×	×	×	3
4500-SiO_2 D	×	×	×	3
4500-SiO_2 E	×	×	×	3
4500-SiO_2 F	×	×	×	3
4500-S^{2-} D	×	×	×	3
4500-S^{2-} E	×	×	×	3
4500-S^{2-} F	×	×	×	3
4500-S^{2-} G	×	×	×	3
4500-S^{2-} I	×	×	×	3
4500-S^{2-} J	×	×	×	3
4500-SO_3^{2-}B	×	×	×	3
4500-SO_3^{2-}C	×	×	×	3
4500-SO_4^{2-} C	×	×	×	3
4500-SO_4^{2-} D	×	×	×	3
4500-SO_4^{2-} E	×	×	×	3
4500-SO_4^{2-} F	×	×	×	3
4500-SO_4^{2-} 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_2 4500-CO_2.D.
5. Additional QC check with pH standard whose value is bracketed by calibration standards.
6. Zero check with zero oxygen sample.
This table is not comprehensive; refer to the specific method and 4020B for further details.

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, revision 1.11. 40 CFR Part 136, Appendix B. *Fed. Reg.* 5:23703.