2020

QUALITY ASSURANCE/QUALITY CONTROL

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2020 A. INTRODUCTION

Quality control (QC) is an important attribute of any laboratory's quality assurance (QA) program. Without QC, 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 (MDL) or quantification limit], 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 QA manual and standard operating procedures. In addition, it is the laboratory's responsibility to qualify and report data values not meeting QC or other method-defined requirements with sufficient information so the client or end user can determine the usability of the qualified data.

While general information on QC procedures is provided in Part 1000 and specific procedures are typically outlined in individual methods, some of the methods in Part 2000 are not amenable to standard QC procedures; they have procedures considered unique to the method that do not necessarily apply to other more conventional analytical methods. For some methods, such as oxygen-consumption rate, bias is not applicable. Several methods in this part do not have acceptance-criteria guidance for either precision or bias of test results. This does not, however, relieve analysts of the responsibility for evaluating the test's accuracy and precision. Laboratories should generate method-specific acceptance criteria for precision or bias (or both) using control-charting techniques.

Evaluate precision by analyzing duplicate samples. However, if these results are "nondetect" or "invalidated," precision cannot be calculated. Laboratory-fortified matrices (LFMs) are not applicable to methods currently in Part 2000, so Table 2020:2 has no entry in the LFM column.

Evaluate bias by analyzing standards or samples with known or certifiable parameter values. If a known or certifiable standard analyte cannot be prepared or is otherwise unavailable, then bias cannot be calculated.

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 and accreditation.

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.

2020 B. Quality Control Practices

1. Initial Quality Control

a. Initial demonstration of capability (IDC): Analysts must demonstrate their capability to use a method before analyzing any samples for the first time using that method. For methods in which bias is applicable (see Table 2020:1), run a laboratory-fortified blank (LFB) (2020 B.2*e*), performance evaluation sample, or standard with a known or otherwise certifiable concentration at least 4 times and compare results to the limits listed in the method or those established by the laboratory. If

Table 2020:1. Methods in Part 2000 Indicating or Amenable to Initial Quality Control

	Section	Bias	Precision	MDL	Operational Range
2120 B	Color	–	•	–	–
2120 C		–	•	•	–
2120 D		–	•	•	–
2120 E		–	•	•	–
2120 F		–	•	•	–
2130 B	Turbidity	–	–	•	–
2170 B	Flavor Profile Analysis	–	•	–	–
2310 B	Acidity	–	•	–	–
2320 B	Alkalinity	•	•	–	–
2340 C	Hardness	•	•	–	–
2350 B	Oxidant Demand/Requirement	–	–	•	–
2350 C		–	–	•	–
2350 D		–	–	•	–
2350 E		–	–	•	–
2510 B	Conductivity	–	•	–	–
2520 B	Salinity	–	•	–	•
2520 C		–	•	–	–
2530 C	Floatables	•	•	•	–
2540 B	Solids	–	•	–	–
2540 C		–	•	–	–
2540 D		–	•	–	–
2540 E		–	•	–	–
2560 B	Particle Counting and Size Distribution	–	•	•	–
2560 C		–	•	•	–
2560 D		–	•	•	–
2570 B	Asbestos	•	•	–	–
2580 B	Oxidation–Reduction Potential	•	•	–	–
2710 G	Tests on Sludges	–	•	–	–
2710 H		–	•	–	–
2720 B	Anaerobic Sludge Digester Gas Analysis	•	•	–	–
2720 C		•	•	•	–
2810 B	Dissolved Gas Supersaturation	•	•	–	–

• indicates that the QC type is considered applicable or amenable to the method.
– indicates that the QC type is neither applicable or amenable to the method.
Note: This table is not comprehensive; refer to the specific method for details.

no limit is specified, use the following procedure to establish limits:

Calculate the standard deviation of the 4 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 *t* factor for 99% confidence limits and 3 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 Sections 1020 B.1 and 2)

b. Method detection level (MDL): Before analyzing samples, determine the MDL for each analyte or method parameter in accordance with Section 1020 B.4. Part 2000 methods considered amenable to MDL determination are indicated in Table 2020:1. Determine MDL at least annually for each analyte or parameter in a method and major matrix category. The laboratory should define all matrix categories in its QA manual.

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

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 or other test response. The minimum reporting level (MRL) is set to a concentration at or above the lowest standard used in the analysis. Quantitation at the MRL must be verified initially and at least quarterly (preferably daily) by analyzing a QC sample (where applicable to the method). Laboratories should define acceptance criteria for the operational range, including MRL, in the QA/QC documentation. In Part 2000, only salinity suggests an initial operating range (see Table 2020:1).

2. Ongoing Quality Control

a. Calibration or standardization: Calibrate the method or standardize titration reagents using the directions in the procedure. Methods in Part 2000 that require calibration or titration reagent standardization are indicated in Table 2020.2. (For basic calibration guidance, see Section 1020 B.11.)

b. Calibration or standardization verification: Verify calibration by periodically analyzing a calibration standard and calibration blank during a run—typically, after each batch of 10 samples and at the end of the run. The calibration verification standard's analyte or parameter 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. The first step may be to reanalyze the calibration verification. If the calibration verification passes, continue the analysis. Otherwise, repeat the initial calibration and reanalyze the 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 midlevel second-source calibration standard whenever a new initial calibration curve is prepared. Results must agree within 15% (unless otherwise specified in a method).

Verify standardized titration reagents by periodically re-standardizing. Method parameters in Part 2000 that are determined using standardized titration reagents are acidity, alkalinity, and hardness. Typically, the standardized reagents are stable for several months when sealed to avoid evaporation and stored properly. Re-standardize reagents once a month or when improper storage occurs. If the titration reagent's normality (titer value) has changed, then use the measured value, adjust the normality (titer value) as the procedure describes, or prepare and standardize fresh titration reagent as needed.

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. Methods in Part 2000 considered amenable to QCS determination are indicated in Table 2020.2.

d. Method blank (MB): Include at least one MB daily or with each batch of 20 or fewer samples, whichever is more frequent. Any constituents 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 1020 B.5. This may include reanalyzing the sample batch.

e. Laboratory-fortified blank (LFB): If each initial calibration solution is verified via a second source (2020 B.2*b*), the LFB need not be from a second source (unless otherwise specified in a method). Table 2020:2 indicates methods in Part 2000 where the use of LFB is considered appropriate.

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 1020 B.13) for these measurements to demonstrate ongoing capability. Some methods may have specific limits to use in lieu of plotting control charts. In those cases, 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 2020:2), randomly select routine samples to be analyzed twice. Independently prepare and analyze duplicate samples. 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

Table 2020:2. Summary of Ongoing Quality Control for Methods in Part 2000

	Section	Calibrate or Standardize	QCS	MB	LFB	Duplicates	LFM
2120 B	Color	•	•	–	–	•	–
2120 C		•	•	–	–	•	–
2120 D		•	•	–	–	•	–
2120 E		•	•	–	–	•	–
2120 F		•	•	–	–	•	–
2130 B	Turbidity	•	•	–	–	–	–
2150 B	Odor	–	–	•	–	–	–
2150 C		–	–	•	–	•	–
2160 B	Taste	–	–	•	–	–	–
2170 B	Flavor Profile Analysis	–	–	•	–	•	–
2310 B	Acidity	•	•	•	•	•	–
2320 B	Alkalinity	•	•	–	•	•	–
2340 C	Hardness	•	•	•	•	•	–
2350 B	Oxidant Demand/Requirement	–	–	•	–	–	–
2350 C		–	–	•	–	–	–
2350 D		–	–	•	–	–	–
2350 E		–	–	•	–	–	–
2510 B	Conductivity	•	•	–	•	•	–
2520 B	Salinity	•	•	–	•	•	–
2520 C		•	•	–	–	•	–
2540 B	Solids	–	–	•	•	•	–
2540 C		–	–	•	•	•	–
2540 D		–	–	•	•	•	–
2540 E		–	–	•	•	•	–
2540 F		–	–	–	–	•	–
2540 G		–	–	–	–	•	–
2550 B	Temperature	•	–	–	–	–	–
2560 B	Particle Counting and Size	•	•	•	•	•	–
2560 C	Distribution	•	•	•	•	•	–
2560 D		•	•	•	•	•	–
2570 B	Asbestos	•	–	•	–	•	–
2580 B	Oxidation–Reduction Potential	•	–	–	–	•	–
2710 B	Tests on Sludges	•	–	–	–	–	–
2710 G		–	–	–	–	•	–
2710 H		–	–	–	–	•	–
2720 B	Anaerobic Sludge Digester Gas	–	–	–	–	•	–
2720 C	Analysis	•	•	–	–	•	–
2810 B	Dissolved Gas Supersaturation	•	–	–	–	•	–

• indicates that the QC type is considered applicable or amenable to the method.
– indicates that the QC type is neither applicable or amenable to the method.
Note: This table is not comprehensive; refer to the specific method for details.

limits are not provided. (For basic guidance on duplicates, see Section 1020 B.7.) Some regulatory programs require more frequent use of duplicates.

3. Calculations

a. LFB recovery:

$$\text{LFB \%Recovery} = \left[\frac{measured\ conc}{spiked\ conc}\right] \times 100$$

b. Relative percent difference:

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

where:

D_1 = concentration determined for first duplicate, and
D_2 = concentration determined for second duplicate.

c. Relative standard deviation (% RSD):

$$\%\ \text{RSD} = \frac{s}{\bar{x}} \times 100$$

$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{(n-1)}}$$

where:

s = standard deviation,
n = total number of values from replicate analyses,
x_i = each individual value used to calculate mean, and
$\bar{x}$ = mean of the total number (n) of values.

References

1. Meier PC, Zund EE. Statistical methods in analytical chemistry, 2nd ed. New York, (NY): Wiley Interscience; 2000.
2. U.S. Environmental Protection Agency. Definition and procedure for the determination of the method detection limit, rev. 1.11, 1995. 40 CFR Part 136, Appendix B. Fed Reg. 5:23703.

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