6020 Quality Assurance/Quality Control

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6020 A:2024 INTRODUCTION TO LABORATORY QA/QC ACTIVITIES

Every laboratory that analyzes environmental water and wastewater samples for chemical contaminants must operate under a quality management system (QMS), which establishes the basis for the laboratory's quality assurance (QA) and quality control (QC) activities. The QMS sets forth requirements for laboratory operations that specify the planned and systematic measures and activities required to produce reliable data with known and documented precision and accuracy.[1] QMS standards commonly implemented at laboratories include *Quality Systems for Chemical Testing* (Volume 1 of the *TNI Standard*)[2] and *General Requirements for the Competence of Testing and Calibration Laboratories*[3] (ISO/IEC 17025). *The Manual for the Certification of Laboratories Analyzing Drinking Water—Criteria and Procedures, Quality Assurance*[4] addresses QA/QC requirements established by the US EPA for Safe Drinking Water Act (SDWA) compliance testing. Part 1000 provides the minimum requirements for establishing QA and QC practices for methods in Part 6000.

The laboratory's QMS includes the laboratory's standard operating procedures (SOPs). It addresses default QC measures applicable to instrument calibration and batch QC requirements for precision and bias (accuracy) of analytical measurements. Quality control results render meaningful the results of analytical tests. The details of the QC procedures, their frequency, and expected ranges of results are formalized in a written Quality Assurance Manual, SOPs, or both.

Some of the methods in Part 6000 include specific QC procedures, frequencies, and acceptance criteria. These are considered the minimum quality controls needed to perform the method successfully; additional QC procedures are often needed. If the QC criteria listed in this section exceed those listed in the individual methods, the criteria in this section must also be included. Some regulatory programs may require further QC or have alternative acceptance limits.

REFERENCES

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2. Management and Technical Requirements for Laboratories Performing Environmental Analysis, Vol. 1. Weatherford, Texas: The NELAC Institute; 2016.
3. International Standards Organization; International Electrotechnical Commission. ISO/IEC 17025. General requirements for the competence of testing and calibration laboratories. Geneva, Switzerland: 2017.
4. Manual for the Certification of Laboratories Analyzing Drinking Water—Criteria and Procedures, Quality Assurance, 5th ed. EPA-815-R05-004. Cincinnati (OH): U.S. Environmental Protection Agency; 2005.

6020 B:2024 LABORATORY QC PRACTICES

At a minimum, include in the laboratory's QC program integrated QC practices that address basic instrument and analyst performance, initial and ongoing calibrations, and the precision and bias (accuracy) of each method (as measured using batch QC samples). The description of these practices are separated into two sections: practices that relate to initial and on-going method and analyst performance and those practices that are specific to a batch of samples.

QC practices that relate to initial analyst and method performance include:

- Initial demonstration of capability (IDC) (also referred to as initial precision and recovery (IPR)
- Ongoing demonstration of capability (ODC)
- Method detection limit (MDL)
- Minimum reporting limit (MRL) [also referred to limit of quantitation (LOQ), reporting limit (RL), or minimum level (ML)]
- Instrument calibration, including initial calibration (ICAL), initial calibration verification (ICV) and continuing calibration verification (CCV) single-blind QC check sample (blind to the analyst) or double-blind QC check sample (blind to the laboratory, also known as a proficiency test (PT) sample

Each analytical method or SOP typically includes the minimum required batch QC for each analysis. A comprehensive QC program consists of at least the following elements, as applicable:

- Method blank (MB)
- Laboratory-fortified blank (LFB) [also referred to as blank spike or laboratory control sample (LCS) or ongoing precision and accuracy (OPR)], including an optional low-level LFB
- Laboratory-fortified matrix (LFM) (also referred to as matrix spike)
- Laboratory-fortified matrix duplicate (LFMD) (also referred to as matrix spike duplicate) or duplicate sample (DS)
- Internal standard (IS)
- Surrogate spike (SS)
- Extracted internal standard (EIS), for isotope dilution methods
- Mass calibration (MS)
- Method-specific QC practices

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Note: If contamination is observed or detected, the laboratory may find it useful to conduct analyses on other types of blanks including field blanks, trip blanks, storage blanks, or instrument blanks to try and ascertain the source of the contamination. See 6020 B.6.

1. INSTRUMENT CALIBRATION AND CALIBRATION VERIFICATION

a. Initial calibration: Except for isotope dilution methods, perform initial calibration using at least 4 concentrations of standards if average response factor is used, 5 concentrations of standards for linear curves, or at least 6 concentrations of standards for nonlinear curves. Set the lowest standard concentration as the MRL. The highest concentration standard defines the upper end of the calibration range. The calibration range should encompass the analytical concentration values expected in samples, but this may be constrained by instrumental limitations. Choose calibration standard concentrations with no more than one order of magnitude between concentrations. A variety of calibration functions may be appropriate: response factor (RF) for internal standard calibration, calibration factor (CF) for external standard calibration, or calibration curve. Calibration curves may be linear or nonlinear either through or not through the origin. 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.

For isotope dilution methods, a single-point calibration may be used for the extracted internal standard (EIS) as long as the concentration is equal to the amount of the EIS spiked into the sample. However, this practice is not recommended for those EISs that exhibit very low recoveries because a significant bias may be introduced. Addition of EIS spikes to extracts in samples that have been diluted is not recommended since the recovery of the original EIS spike is unknown.

Note: EPA Method 8000 D provides excellent background information on various approaches to instrument calibration, including external standard, internal standard, and isotope dilution techniques as well as a discussion of the various models used to generate calibration curves such as linear regression and second- and third-order calibration curves.[1]

If using response factors (internal standard) or calibration factors (external standard), evaluate the instrument's performance or sensitivity for the analyte of interest against minimum acceptance values. The calculated relative standard deviation (RSD), expressed as a percentage, for each analyte of interest must be less than the method-specified value. Refer to the method being used for the calibration procedure and acceptance criteria on the response or calibration factors for each analyte. Use 30% if a method does not have published acceptance criteria.

If a regression curve is used, whether linear or nonlinear, compare each calibration point to the curve by calculating either relative error (RE) or relative standard error (RSE). If any recalculated concentration is not within the method's acceptance criteria, identify the source of any outlier and correct before sample quantitation. Some Part 6000 methods still allow for the use of correlation coefficient (r) or coefficient of determination (r^2) to evaluate the "goodness" of the curve. This practice is now well-known to be inappropriate for instrument calibrations and must not be used.[2]

An initial calibration with any of the above functions (response factor, calibration factor, or calibration curve) is used to quantitate the analytes of interest in samples. A continuing calibration verification (CCV) is performed only to check, or verify, the initial calibration. Perform initial calibration when the instrument is set up and whenever CCV criteria are not met.

If the criteria for the ICAL are not met, samples may not be analyzed until an acceptable ICAL is generated. Corrective actions include performing instrument maintenance, removing calibration points from either the low or high end thus reducing the operational range, or replacing one of the calibration standards if the problem appears to be associated with a particular standard. The selective removal of individual calibration points solely to meet quality control acceptance criteria is prohibited.[3]

b. Initial calibration verification: The laboratory must verify the accuracy of its initial calibration standard by analyzing a midlevel second-source calibration standard whenever a new initial calibration curve is prepared. Results must agree within 10% unless otherwise specified in a method. A second-source standard is one from another vendor or a completely different lot from the same vendor. If neither option is feasible, then the second-source calibration standard must be prepared from primary stock materials by a different analyst.

c. Continuing calibration verification: Analysts must periodically use a calibration standard to confirm that instrument performance has not changed significantly since initial calibration. Base the frequency of the verification on time (e.g., every 12 h) or on the number of samples analyzed (e.g., after every 20 samples). Verify calibration by analyzing one 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 the reanalysis of any affected samples. Refer to the method being used for the frequency of and acceptance criteria for calibration verification.

If a CCV fails, if possible, immediately cease analyzing samples and take corrective action. Often, the problem can be fixed by performing injector maintenance or trimming a few centimeters from the front of the column. Then, reanalyze the CCV. If the calibration verification passes, continue the analysis. Otherwise, repeat the initial calibration and reanalyze any samples that have been run since the last acceptable calibration verification.

For methods that use calibration factors (external standard), a CCV is required at the beginning and end of each analytical batch.

d. Calculations:

1) Response factor (RF):

$$RF = (A_s \times C_{is})/(A_{is} \times C_{is})$$

where:

A_s = area for the analyte of interest or surrogate,
A_{is} = area for the internal standard,
C_{is} = concentration of the internal standard (µg/mL), and
C_s = concentration of the analyte of interest or surrogate (µg/mL).

2) Calibration factor (CF)

$$CF = \frac{A_s}{C_s}$$

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where:

C_s = concentration of the analyte in the standard (ng/mL) and
A_s = peak height or area.

3) Relative Error (RE)

$$\%\ Relative\ error = \frac{x_i' - x_i}{x_i} \times 100$$

where:

x_i = true value for the calibration standard
x_i' = measured concentration of the calibration standard

4) Relative standard error (RSE):

$$\%\ RSE = 100 \times \sqrt{\sum_{i=1}^{n}\left[\frac{x_i' - x_i}{x_i}\right]^2 \Big/ (n-p)}$$

where:

x_i = true value of the calibration level i,
x_i' = measured concentration of calibration level I,
p = number of terms in the fitting equation (average = 1, linear = 2, quadratic = 3), and
n = number of calibration points.

2. INITIAL DEMONSTRATION OF CAPABILITY (IDC)

Each analyst in a laboratory must conduct an initial demonstration of capability (IDC) before analyzing any field samples to demonstrate proficiency in performing the method and obtaining acceptable results for each analyte. The IDC is also used to demonstrate that the laboratory's modifications to a method produce results as precise and accurate as those produced by the reference method. One way to perform an IDC is to analyze a method blank and at least 4 LFBs at a concentration between 2 times the MRL and the midpoint of the calibration curve (or other level specified in the method). Run the IDC after analyzing all required calibration standards. Ensure that the method blank does not contain any analyte of interest at a concentration greater than half the MRL (or other level specified in the method). Calculate the precision RSD and accuracy (average percent recovery) and compare to acceptance limits in the method. Another option is to obtain acceptance criteria from a PT sample provider on the inter-laboratory PT studies and translate the data to percent recovery limits per analyte and method being used.

If any individual RSD exceeds the precision limit or any individual analyte recovery falls outside the range for recovery, system performance is unacceptable for that compound. Correct the problem and repeat the test.

In the absence of established mandatory criteria, generally acceptable guidelines for percent recovery are 70% to 130% and an RSD criterion of 30%. Wider laboratory-generated limits may be used if acceptable to the customer.

3. ONGOING DEMONSTRATION OF CAPABILITY (ODC)

Any analyst must demonstrate on-going capability by routinely meeting the QC requirements of the method, laboratory SOP, client specifications, and Method 6020. If the method has not been performed by the analyst in a 12-month period, a new IDC must be performed.

This on-going demonstration may be one of the following:

a) acceptable performance of a blind sample (single blind to the analyst) or successful analysis of a blind proficiency test sample that contains the analytes of interest;
b) another IDC;
c) at least 4 consecutive LFB samples with acceptable levels of precision and accuracy;
d) a documented process of reviewing QC samples performed by an analyst or groups of analysts relative to the QC requirements of the method, laboratory SOP, or client specifications. This review can be used to identify patterns for individuals or groups of analysts and determine whether corrective action or retraining is necessary;
e) if a) through d) are not technically feasible, then analysis of real-world samples with results within a pre-defined acceptance criterion (as defined by the laboratory or method) must be performed.

4. METHOD DETECTION LIMIT

Before analyzing samples, determine the MDL for each analyte of interest and method to be used according to the EPA procedure published in 40 CFR Part 136 Appendix B. Some test methods are not amenable to MDL determinations; in such cases, refer to each method to determine reporting levels.[4]

As a starting point for selecting the concentration for determining the MDL, use an estimate of 5 times the estimated true detection level. Start by adding the known amount of constituent to reagent water or sample matrix to achieve the desired concentration. Prepare and analyze at least 7 portions of this solution over a minimum 3-day period to ensure that the MDL determination is more representative of routine measurements in the laboratory. The replicate measurements should be in the range of 2 to 5 times the estimated MDL. Calculate the estimated standard deviation, *s*, of the replicates, and from a table of one-sided *t* distribution, select *t* for the appropriate number of replicates at the 99% confidence level. This value is then multiplied by the standard deviation to calculate the spiked samples MDL or MDL_S:

$$MDL_S = s * t$$

Ideally, estimate *s* using pooled data from several analysts rather than data from one analyst (if the laboratory routinely has multiple analysts running a given test method). For specific information on pooling, see Section 1020 B.4.

Perform MDL determinations iteratively. If the calculated MDL is not within a factor of 10 of the known addition, repeat determinations at a more suitable concentration. Verify the MDL on an ongoing basis (at least quarterly) for each analyte, major matrix category, and method in use at the laboratory if any samples were analyzed by that method during the quarter. Verify MDL determination for each instrument, as well as whenever significant modification to the method's instrument or operating conditions also modifies detection or chemistry. Include all sample-preparation steps in the MDL determination.

Analyze 7 blank samples over at least 3 days based on the procedure outlined by the US Environmental Protection Agency.[4] In addition to calculating the MDL_S, calculate the MDL based on the blanks, or MDL_b, as follows.

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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 blanks 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

$$MDL_b = X + tS_b$$

where:

X = mean of blank results (set negative mean values to 0),
t = the Student t value for the number of blanks, and
S_b = sample standard deviation of the blank results.

The MDL is the greater of the two results obtained from the MDL_s and MDL_b calculations.

When analyzing more than 7 samples to determine the MDL_s and MDL_b, correct the critical t-distribution value from 3.14 using the Student t distribution table for 99% confidence (one tail) and n – 1 degrees of freedom.

The MDL must be verified at least quarterly by analyzing LFB (subjected to all sample-preparation steps) spiked at or below the MRL. If the method is altered in a way other than routine maintenance and the change can be expected to elevate the detection limit, then a spike at or below the MRL concentration and a blank must be prepared and analyzed. If the spike gives a result that meets the qualitative identification criteria and the concentration is above zero, and the blank gives a result below the MDL, then the MDL is verified. If not, the MDL must be re-determined.

Generally, apply the MDL to reporting sample results as follows (unless there are regulatory or client constraints to the contrary):

- Report results below the MDL as "not detected" (ND) or <MDL (where MDL is replaced by the numerical value of the MDL).
- Report results between the MDL and MRL (e.g., LOQ, ML) with qualification that the value is below the LOQ for the quantified value given.
- Report results above the LOQ with a value (and its associated uncertainty if required).

5. MINIMUM REPORTING LEVEL AND OPERATIONAL RANGE

The laboratory must establish a Minimum Reporting Level (MRL), which is the lowest concentration at which quantitative data are to be reported. The MRL can be established using any of the procedures below:

- The concentration of the lowest calibration standard
- 3 times the MDL[5]
- 3.18 times the MDL rounded to the nearest 1, 2, or 10[6]

Quantitation at the MRL must be verified initially and at least quarterly by analyzing LFB (subjected to all sample-preparation steps) spiked at a level at or below the MRL. A successful verification meets a method's or laboratory's accuracy requirements at the MRL. Note: The MDL and MRL verification can be performed at the same time with one low-level spike.

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 known concentrations that provide increasing instrument response. Laboratories must define acceptance criteria for the operational range in their QA documentation.

6. BLANKS

A *method blank* (consists of reagent water and all reagents (including preservatives) that normally are in contact with a sample during the entire analytical procedure. The method blank is used to determine whether, and the extent to which, reagents and the preparative analytical steps contribute to measurement uncertainty. At a minimum, include one method blank with each sample set (batch) or on a 5% basis, whichever is more frequent. Analyze a blank after the daily calibration standard. Evaluate reagent blank results for contamination. If unacceptable contamination is present in the reagent blank, identify and eliminate the source. Typically, sample results are suspect if analytes in the reagent blank are greater than the MRL. Samples analyzed with a contaminated blank must be reprepared and reanalyzed. Refer to the method being used for specific method blank acceptance criteria. General guidelines for qualifying sample results with regard to method blank quality are as follows:

- If the method blank is less than the MDL and sample results are greater than the MRL, then no qualification is required.
- If the method blank is greater than the MDL but less than the MRL and sample results are greater than the MRL, then qualify the results to indicate that the analyte was detected in the method blank.
- If both the method blank and sample result are above the MDL and below the MRL, correct the source of contamination and reanalyze the affected samples or qualify the data.
- If the method blank is greater than the MRL, further corrective action or qualification is required.

Equipment, field, trip, storage, and instrument blanks, although not generally required, may be useful to identify the source of contamination.

- An equipment blank is laboratory clean water sent to the sampling location taken through the sampling process, including any sampling devices, tubing, or filters. This blank can thus identify the sampling equipment as a source of contamination.
- A field blank is laboratory clean water sent to the sampling location and then transferred to a different sample container. This blank can thus identify ambient conditions (e.g., smoking, sunscreen, insect repellant) as a source of contamination.
- A trip blank is laboratory clean water sent to the field and then returned unopened. This blank can be used to identify contaminants that might arise from the shipping process.
- A storage blank is laboratory clean water stored under the identical conditions as the sample and thus may be used to identify storage conditions that resulted in a contamination.
- An instrument blank consists of a calibration solution that is not spiked with any analytes and can be used to identify if reagents are the source of a contamination.

7. LABORATORY-FORTIFIED BLANK (LFB)

A *laboratory-fortified blank* is a reagent water sample to which a known concentration of the analytes of interest has been added. An LFB is used to evaluate laboratory performance and analyte recovery in a blank matrix. At a minimum, include one LFB with each sample set (batch) or on a 5% basis, whichever is more frequent. Process the LFB through all sample preparation and analysis steps. Use an added concentration of at least 2 times the MRL, less than or equal to the midpoint of the calibration curve,

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or a level specified in the method. Evaluate the LFB for percent recovery of the added analytes by comparing the results to the method-specified limits, control charts, or other approved criteria. If LFB results are out of control, take corrective action, including repreparation and reanalysis of associated samples if required. If repreparation and reanalysis is not feasible (e.g., no sample available or expired holding times), qualify the data as described in 6020 C. Use LFB results to evaluate batch performance, calculate recovery limits, and plot control charts (see 1020 B.13).

a. Allowable marginal exceedances: If a large number of analytes are in the LFB, it becomes statistically likely that a few will be outside control limits. This may not indicate that the system is out of control; therefore, corrective action may not be necessary. Upper and lower marginal exceedance (ME) limits can be established to determine when corrective action is necessary. A ME is defined as being beyond the LFB control limit (3 standard deviations) but within the ME limits. ME limits are between 3 and 4 standard deviations of the mean. The number of allowable marginal exceedances is based on the number of analytes in the LFB. If more analytes exceed the LFB control limits than are allowed or if any one analyte exceeds the ME limits, the LFB fails and corrective action is necessary. This marginal exceedance approach is relevant for methods with long lists of analytes. It does not apply to target analyte lists with fewer than 11 analytes.

Refer to Table 6020:1 for the number of allowable marginal exceedances.

If the same analyte exceeds the LFB control limit consecutively, it is an indication of a systemic problem. The source of the error must be located and corrective action taken. Laboratories must have a written procedure to monitor the application of marginal exceedance allowance to the LFB, which must include how the laboratory determines what constitutes a consecutive failure.

A *low-level LFB* fortified at 2 to 5 times the MDL may be used as a check for false negatives and for MDL/MRL verification. Control limits for low-level LFB may be variable, depending on the method but are typically expected to be 50% to 150%. Depending on the method's specific requirements, prepare the addition solution from either the same reference source used for calibration or from an independent source.

b. Calculation of 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.

Table 6020:1. Number of Analytes with Allowable Marginal Exceedance Based on Number of Analytes in the LFB

Number of Analytes in LFB	Number Allowed as Marginal Exceedances
>90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
<11	0

LFB = laboratory fortified blank

8. LABORATORY-FORTIFIED MATRIX

A *laboratory-fortified matrix* (LFM) is a separate portion of a sample to which a known amount of the analytes of interest are added before sample preparation.

a. The LFM is used to evaluate analyte recovery in a sample matrix. If a 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. An LFM analysis can only be performed if the laboratory is provided an adequate volume of sample. Add a concentration that is at least 10 times the MRL, less than or equal to the midpoint of the calibration curve, or at a method-specified level, to the selected samples. Prepare the LFM from the same reference source used for the LFB. If the sample contains no detectable analyte of interest or when the analyte level is unknown but expected to be near the MRL, adjust the LFM concentration to no more than 5 times the MRL to ensure that the selected sample's level does not adversely affect recovery. If the sample is known or expected to contain the analyte of interest, then add approximately as much analyte to the LFM sample as the concentration expected to be found in the known sample. Evaluate the results obtained for LFMs for accuracy or percent recovery. If LFM results are out of control, then take corrective action to rectify the matrix effect, use another method, or qualify the data if reported. Refer to the method being used for specific acceptance criteria for LFMs until the laboratory develops statistically valid, laboratory-specific performance criteria. Base sample batch acceptance on results of LFB analyses rather than LFMs alone, because the LFM sample matrix may interfere with method performance.

b. Calculation:

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

9. LABORATORY-FORTIFIED MATRIX DUPLICATE OR DUPLICATE SAMPLES

Duplicate samples are analyzed randomly to assess precision on an ongoing basis.

a. LFM duplicate: If an analyte is rarely detected in a matrix type, use an LFM duplicate. An *LFM duplicate* is a second separate portion of the sample described in 6020 B.8 to which a known amount of the analytes of interest are added before sample preparation. If sufficient sample volume is collected, this second portion of sample is processed in the same way as the LFM. If there is not enough sample for an LFM duplicate, then use a portion of a different sample (duplicate) to gather data on precision. At 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). 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 qualify the data if reported. If duplicate results are out of control, then re-prepare and reanalyze

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the sample and take additional corrective action, as needed. When the value of one or both duplicate samples is less than or equal to 5 times the MRL, the laboratory may use the MRL as the control limit, and the duplicate results are not used. Refer to the method being used for specific acceptance criteria for LFM duplicates or duplicate samples until the laboratory develops statistically valid, laboratory-specific performance criteria. If the method being used does not provide limits, calculate preliminary limits from the IDC. Base sample batch acceptance on results of LFB analyses rather than LFM duplicates alone, because the LFM sample matrix may interfere with method performance.

b. Duplicate samples: Using duplicates is appropriate when there is a high likelihood that the compounds of interest are present in the sample, particularly at high concentrations that make spiking difficult. Methods in this section routinely use LFMDs. Process duplicate samples independently through the entire sample preparation and analysis. Include at least one duplicate for each matrix type each day samples are prepared or with each preparation batch of 20 or fewer samples. Calculate control limits for duplicates when method-specific limits are not provided. Some regulatory programs require more frequent use of duplicates.

c. Calculation of relative percent difference (RPD):

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

or

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

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.

10. INTERNAL STANDARD

An *internal standard* is a compound not expected to occur naturally in field samples; it is included in each standard and added to each sample or sample extract just before sample analysis. Internal standards must mimic the analytes of interest and not interfere with the analysis. Choose an internal standard whose retention time or mass spectrum is separate from the analytes of interest and that elutes in a representative area of the chromatogram. Internal standards are used to monitor retention time, calculate relative response, or quantify the analytes of interest in each sample or sample extract. When quantifying by the internal standard method, measure all analyte responses relative to this internal standard.

Many methods that use internal standard calibration include acceptance limits for responses of the internal standards in the calibration standards, samples, or both. Those limits are typically expressed in terms of peak areas because the concentration of the internal standard cannot be measured directly (i.e., one has to assume that the entire mass injected into the sample or sample extract is present during analysis). Common consensus limits are 50% to 200% of the area of the internal standard in the most recent calibration standard. Representing a factor of two, these limits are used as a gross diagnostic check on addition of the internal standards to the samples or extracts and injection of the sample aliquot into the instrument.

Samples that have internal standard areas less than 50% or greater than 200% of the most recent calibration standard indicate a matrix effect or other issue and an alternate technique (e.g., a different internal standard or an external standard calibration) must be conducted.

11. SURROGATE SPIKES

A *surrogate spike* is a known amount of a unique compound added to each sample before extraction. Surrogates mimic the analytes of interest and are compounds unlikely to be found in environmental samples (e.g., fluorinated compounds or stable, isotopically labeled analogs of the analytes of interest). Surrogates are introduced to samples before extraction to monitor extraction efficiency and percent recovery in each sample. Surrogates may not be appropriate for some methods.

a. Calculate percent recovery and determine control limits (Section 1020 B) for these measurements. Some methods may have specific limits to use in lieu of calculating control limits. If so, control charts may still be useful in identifying potential problems but are not required. Ensure that surrogate recoveries meet the method's performance criteria (when such criteria are specified) or the laboratory-generated limits. Failures may indicate analytical problems or problems tied to the sample matrix. If surrogate results are out of control, then take corrective action, including repreparation and reanalysis if possible, or reporting the data with qualifiers.

b. Surrogate recovery:

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

where:

C_b = surrogate concentration determined experimentally and
I = initial concentration of surrogate added to sample.

12. EXTRACTED INTERNAL STANDARD

a. **An *extracted internal standard*** (EIS) is an isotopically labeled analogue of the analyte being measured. The EIS is added to the sample before sample preparation. The concentration of the analyte being measured is based on a direct comparison of the area of a particular ion in the EIS to the corresponding ion in the analyte being measured, in effect providing a recovery correction factor.

For methods that use this approach, the recovery of the EIS should be assessed using reasonable criteria such as 70% to 130%.

b. Isotope dilution calculation:

$$C_s = \frac{A_s}{A_{eis}} \times C_{eis}$$

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where:

C_s = concentration of the analyte in the sample,
A_s = peak area of analyte,
A_{eis} = peak area of extracted internal standard, and
C_{eis} = concentration of the extracted internal standard in the sample.

13. MASS CALIBRATION

For methods that use mass spectrometry, tune the instrument so that it delivers the correct masses at the correct relative responses. Follow tuning criteria established in the reference method or by the manufacturer.

14. PROFICIENCY TESTING

At least annually (semiannually is recommended) to help verify the accuracy of calibration standards and overall method performance, analyze a single-blind (i.e., blind to the analyst) QC check sample (QCS), ideally provided by an external entity. A double-blind QCS (blind to the laboratory) is called a PT sample. An unacceptable result on a QCS is often a strong indication that a test method is not being followed correctly or that there is some inherent bias, such as inaccurate calibration. Investigate circumstances fully to find the cause. In many jurisdictions, participation in PT studies is a required part of laboratory certification or accreditation.

15. METHOD SPECIFIC QC PRACTICES

a. Second column confirmation: Some methods require confirming the identity of analyte via a dissimilar second column. If so, ensure that the phases are dissimilar enough to invert the elution order of some compounds in the analysis or significantly change the pattern of elution if the method involves only a few target analytes. When one column is used solely to quantitate analytes and the other to confirm analyte identification, the confirmation column need not meet all of the method's calibration and QC criteria; however, demonstrate daily that the confirmation column is sensitive enough to identify all compounds at the level being reported. This may be accomplished by analyzing the lowest calibration standard showing adequate signal for all analytes on both columns. Some methods or programs may require quantitative analysis on both columns. If so, the laboratory must meet all QC criteria on both columns. The laboratory must have a procedure that indicates how data are reported when second columns are used (i.e., data always reported from one column, the higher value is reported, or the lower value is reported).

b. Additional instrument checks: Certain methods may require additional QC checks on analytical performance (e.g., endrin/DDT breakdown checks in the analysis of chlorinated pesticides or peak tailing factors). If noted in a method, they are required and must be performed as indicated. However, instrument parameters relating to chromatography (e.g., temperature or gradient ramps and profiles and even column choices) may be optimized as long as all QC and compound identification criteria can be met. All calibration standards, QC samples, and field samples must be analyzed using identical conditions.

16. SPECIFIC QC PRACTICES FOR ALL 6000 SERIES TEST METHODS

Table 6020:2 summarizes the QC practices that are required or optional for each 6000 series test method. Unless otherwise noted, ICAL, ICV, CCV, IDC, ODC, MB, MDL, MRL, LFB, and chromatography checks are required for all methods.

Table 6020:2. Minimum Quality Control for Methods in Part 6000

Topic	Section	LFM	LFMD or DS	IS	SS	EIS	MS	PT	Notes
Taste and odor compounds	6040 B	•	(•)	•	•			(•)	
	6040 C	•	(•)	•	•		•	(•)	
	6040 D	•	(•)	(•)	(•)		•	(•)	
	6040 E	•	(•)	•	•			(•)	
Volatile organic compounds	6200 B	•	(•)	•	•		•	(•)	
	6200 C	•	(•)	•	•			(•)	
Methane	6211 B							(•)	
	6211 C							(•)	
EDB and DBCP	6231 B	•	(•)					(•)	
	6231 C	•	(•)					(•)	
	6231 D	•	(•)					(•)	
THMs and chlorinated organic solvents	6232 B	•	(•)	(•)				(•)	1
	6232 C	•	(•)					(•)	
	6232 D	•	(•)					(•)	
DBPs: HAAs and trichlorophenol	6251 B	•	(•)	•	•			(•)	
DBP: Aldehydes	6252 B	•	(•)	•	•			(•)	2
Extractable base/neutrals and acids	6410 B	•	(•)	•	•		•	(•)	
Pharmaceuticals and personal care products	6810 B	•	(•)	•	•			(•)	1
Phenols	6420 B	•	(•)	•	–		•	(•)	
	6420 C	•	(•)	•	•			(•)	

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Table 6020:2. Continued

Topic	Section	LFM	LFMD or DS	IS	SS	EIS	MS	PT	Notes
PCBs	6431 B	•	(•)	–	•			(•)	
	6431 C	•	(•)	•	•			(•)	
Polynuclear aromatic hydrocarbons	6440 B	•	(•)	–	–			(•)	
	6440 C	•	(•)	•	•			(•)	
Nitrosamines	6450 B	•	(•)	•	•			(•)	1
	6450 C	•	(•)	•	•			(•)	1
Carbamate pesticides	6610 B	•	(•)	(•)				(•)	
Organochlorine pesticides	6630 B	•	(•)		•			(•)	
	6630 C	•	(•)		•			(•)	
	6630 D	•	(•)	•	•			(•)	
Acidic herbicide compounds	6640 B	•	(•)	•	•			(•)	
Glyphosate herbicide	6651 B	•	(•)					(•)	
Tributyltin	6710 B	•		•	•			(•)	
	6710 C	•		•	•			(•)	

LFM = Laboratory-fortified matrix
LFMD = Laboratory-fortified matrix duplicate
DS = Duplicate sample
IS = Internal standard
SS = Surrogate spikes
EIS = Extracted internal standard
MS = Mass calibration
PT = Proficiency testing
• indicates a test is mandatory; (•) indicates a test is optional.
Notes:
1. Additional QC guidelines in method.
2. Second-column confirmation optional.

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6020 C:2024 ADDITIONAL QC PRACTICES

Although not specific QC measures, the following are important activities for a well-managed QC program. (See Section 1020 for more details.)

1. Corrective action and root cause analysis
2. Frequency of QC activities and definitions of a batch
3. QC acceptance criteria, including control charts as applicable
4. Data qualifiers

1. CORRECTIVE ACTION

QC data that are outside the acceptance limits or exhibit a trend are evidence of unacceptable error in the analytical process. Take corrective action promptly to determine and eliminate the source of the error. Do not report data until the cause of the problem is identified and either corrected or qualified (Table 1020:2). Qualifying data does not eliminate the need to take corrective actions but allows analysts to report data of known quality when it is either impossible or impractical to reanalyze the samples. Maintain records of all out-of-control events, determined causes, and corrective action taken. The goal of corrective action is not only to eliminate such events but also to reduce repetition of the causes. Corrective action begins with analysts being responsible for knowing when the analytical process is out of control. Initiate corrective action when a QC check exceeds acceptance limits or exhibits trending, and report an out-of-control event (e.g., QC outliers, hold-time failures, loss of sample, equipment

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malfunctions, and evidence of sample contamination) to supervisors. Recommended corrective actions for unacceptable QC data are as follows:

- Check the data for calculation or transcription error. Correct results if an error occurred.
- Determine whether a sample was prepared and analyzed according to the approved method and SOP. If not, prepare and analyze again.
- Check calibration standards against an independent standard or reference material. If the calibration standards fail, re-prepare calibration standards, recalibrate, or both, and reanalyze affected samples.
- If an LFB fails, analyze another LFB.
- If a second LFB fails, check an independent reference material. If the second source is acceptable, re-prepare and reanalyze affected samples.
- If an LFM fails, check the LFB. If the LFB is acceptable, then qualify the data for the LFM sample, use another method, or use the method of standard addition.
- If an LFM and associated LFB fail, re-prepare and reanalyze the affected samples.
- If a reagent blank fails, analyze another reagent blank.
- If a second reagent blank fails, re-prepare and reanalyze the affected samples.
- If a surrogate or internal standard known addition fails and there are no calculation or reporting errors, re-prepare and reanalyze the affected samples.

2. FREQUENCY OF QC ACTIVITIES

A *preparation batch* is composed of 1 to 20 environmental samples of the same quality systems matrix and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An *analytical batch* is composed of prepared environmental sample extracts which are analyzed together as a group.

Table 6020:3 defines the frequency of each of the QC practices defined in 6020 B.

Table 6020:3. Frequency of Quality Control Practices for Chemical Analysis

QC Practice	Frequency
ICAL	Initially and then any time CCV criteria are not met
ICV	With each ICAL
CCV	At the beginning of each day samples are analyzed[1]
IDC	Once
ODC	Annually
MDL	Once but verified quarterly
MRL	Once but verified quarterly
MB	With each batch
LFB	With each batch
LFM	As specified by the method or client
LFMD	As specified by the method or client
DS	As specified by the method or client
IS	Every sample
SS	Every sample
EIS	Every sample
MS	Daily
PT	At least once per year, preferably twice a year

Note: A closing CCV is required for methods that use external standards.

3. QC ACCEPTANCE CRITERIA

Most promulgated EPA methods have defined acceptance criteria that must be met for any Part 6000 method. Where method defined acceptance criteria don't exist, the laboratory must determine its own criteria. To establish laboratory-generated accuracy and precision limits where none are published, calculate the upper and lower control limits from the mean and standard deviation of percent recovery for at least 20 data points:

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

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

4. DATA QUALIFIERS AND CASE NARRATIVES

If data qualifiers are used to qualify sample results not meeting QC requirements, the data may or may not be usable for the intended purposes. The laboratory must provide the client or end-user of the data with sufficient information to determine the usability of qualified data. Table 6020:4 provides examples of data qualifiers.

An alternative to a data qualifier is to use a case narrative, where the laboratory describes the QC failure, actions taken to correct the problem, and its impact on the reported result. An example of a case narrative is found below:

> In the analysis of wastewater discharge identified as WW-002 outfall for volatile organics, the recovery of the surrogate bromofluorobenzene was 107%, slightly above the upper QC limit of 103%. However, no target compounds were detected in this sample above the MRL so this QC failure did not impact the reported results.

Table 6020:4. Example Data Qualifiers[1]

Data Qualifier	Description
B	Analyte found in reagent blank. Indicates possible reagent or background contamination.
E	Estimated reported value exceeded calibration range.
J	Reported value is an estimate because concentration is less than the reporting limit.
N	Non-target analyte. The analyte is a tentatively identified compound using mass spectrometry.
Q	One or more quality control criteria failed (e.g., LCS recovery, surrogate spike recovery, or CCV recovery).
U	Compound was analyzed for but not detected.

[1] For a thorough discussion of data qualifiers and their use see *National functional guidelines for organic superfund data review. EPA-540/R-20-005. Washington DC: Office of Emergency and Remedial Response, Contract Laboratory Program, U.S. Environmental Protection Agency; 2020.*

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