3020 QUALITY ASSURANCE/QUALITY CONTROL*

3020 A. Introduction

General information and recommendations for quality assurance (QA) and quality control (QC) are provided in Sections 1020 Quality Assurance, 1030 Data Quality, and 1040 Method Development and Evaluation. This section discusses QA/QC requirements that are common to the analytical methods presented in Parts 3000 and 4000. This section is intended to cover a broad range of laboratory needs including, but not limited to, regulatory compliance.

The acceptance limits, frequency of QC activities, and other QA/QC assessment tools are recommended minimum QA/QC activities; refer to individual methods and regulatory program requirements for method-specific QA/QC requirements.

Always consider the overall purpose of analyses. Necessary QA/QC measures and substantiation for operational-control determinations may differ significantly from those for determinations of trace metals at water quality criteria levels. Levels of trace metals in environmental samples may be orders of magnitude lower than in potential sources of contamination.

Use duplicates of samples containing measurable concentrations of analytes of interest, either present in the sample or resulting from fortification (see ¶ 2*g*), to establish precision; calibration checks to determine accuracy; and laboratory-fortified matrix (LFM) recovery to determine matrix interference. Use standards, blanks, calibrations, control charts, the Method of Standard Additions (MSA), and other measurement tools as appropriate. Provide adequate documentation and record-keeping to satisfy client requirements and performance criteria established by the laboratory.

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Joint Task Group: Cindy A. Bamfield (chair), Myriam E. Cardenas, David E. Kimbrough.

3020 B. Quality Control Practices

1. Initial Quality Control

a. Initial demonstration of capability: Verify analyst capability before analyzing any samples and repeat periodically (annually or when there is a new analyst, whichever is more frequent) to demonstrate proficiency with the analytical method. Verify that the method being used provides sufficient sensitivity for the purpose of the measurement (see ¶s 1*b* and 2*e*). Test analyst capability by analyzing at least four well-characterized samples with a concentration of the analyte of interest that is unknown to the analyst.

b. Method detection level (MDL): When required, determine the MDL for each analyte by the procedures of Section 1030C, procedures prescribed by regulatory authorities,[1] or other applicable procedures. For example, the MDL may be determined using multiple analyses during a single-day study, over several days, or alternatively by using quality control samples, e.g., the reporting limit check solution (see ¶ 2*e*) from routine sample analysis batches on an ongoing basis. Instead of analyzing seven or more replicates of a low-concentration laboratory-fortified blank (LFB, see ¶ 2*g* below) on a single day and determining the MDL from the standard deviation of those seven LFBs, the reporting limit check solution (RLCS, see ¶ 2*e* below) may be used from the last seven (or more) routine analyses to determine the standard deviation. Determine MDL annually after the initial determination, as necessary for each analyte and method . Verify MDL for a new analyst or whenever instrument hardware or method operating conditions are substantially modified. The MDL should be less than, or equal to, the reporting limit (see ¶ 2*e* below).

c. Linear dynamic range (LDR): Before using a new method, determine the linear dynamic range (LDR), i.e., the concentration range over which a method has an increasing response to each analyte, by analyzing several standard solutions that bracket the range of interest. The LDR is determined by successive analyses of higher concentration standards until the results are less than 90% of the target value of the standard. Before any analysis, determine LDR as part of the initial demonstration of capability. If a sample has an analyte concentration that is greater than 90% of the determined upper LDR, dilute the sample so that concentration is within the LDR and reanalyze. Verify LDR whenever there are significant changes in instrument conditions or analytical process.

2. Calibration and Quality Control

a. Calibration: Calibrate initially with a minimum of a blank and calibration standard(s) of the analyte(s) of interest. Select calibration standards that bracket the expected concentration of the sample and that are within the method's dynamic range. The number of calibration points depends on the width of the LDR and instrument used. If the number of standards is not specified in the individual method, use a minimum of three standards plus a blank. If multiple standards with a least-squares fit calibration are used, a correlation coefficient of greater than or equal to 0.995 is acceptable. Second-order calibrations are not precluded. Repeat calibration at the beginning of each batch of samples and whenever calibration verification acceptance criteria are not satisfied. If sample results are above the highest calibration point,

confirm by dilution to within the calibration range or, if confirmation is not feasible, flag data as "estimated".

b. Second source calibration verification (SSCV): Prepare a second source check solution (SSCS), also known as a quality control sample (QCS) from a stock solution different from that used to prepare the calibration standard(s), to determine if the stock and working standards are accurate. The measured recovery SSCS should be within a fixed percentage of the expected value. For regulatory compliance purposes, the measured concentration of the SSCS must be between 90 and 110% of the expected value[2,3] except for ICP-AES, which should be between 95% and 105% of the expected value.[4] If the SSCS is not within acceptance limits, do not proceed with analysis; take corrective action such as recalibrating or changing standards. Perform SSCV every time that a new calibration standard is used or once per quarter, whichever is more frequent.

c. Initial calibration verification (ICV): Initial calibration verification is the confirmation that calibration was performed correctly. Verify calibration by analyzing a solution containing the analytes of interest at a concentration within the calibration range. A calibration check solution (CCS) may be prepared from a different stock solution than was used to prepare the calibration standard(s) or from the same stock solution. The measured concentration of the initial calibration verification should be within a fixed percentage of the expected value. For regulatory compliance purposes, use acceptance criteria of between 95% and 105% of the expected value.[4] If the ICV is not within acceptance limits, do not proceed with analysis; take corrective action such as recalibrating or changing standards. If the CCS is prepared from a second source, the SSCV and ICV may be combined into a single step and check solution.

d. Continuing calibration verification (CCV): Continuing calibration verification is the confirmation that instrument response has not changed significantly from the response at initial calibration. Verify calibration by analyzing the calibration check solution (CCS) after every tenth sample. The CCV should be within a fixed percentage of the expected value. If the specific analytical method does not specify acceptance limits for the CCV (e.g., Section 3113), use acceptance criteria of between 90% and 110% of the expected value. If the criteria are not met, repeat calibration and sample determinations since the last acceptable calibration verification. Other corrective actions also may be needed. Use calculated control limits (Section 1020B) to provide better indications of system performance and to provide tighter control limits.

e. Reporting limit verification (RLV): Laboratories often do not report values below a given concentration, usually called a reporting limit or minimum reporting level (MRL). These reporting limits can be set by regulation, by the end-user of the laboratory results, or by the laboratory itself. In any case, verify with each calibration that the instrument is capable of accurately quantifying at the reporting limit. Prepare reporting limit check solution (RLCS) at the reporting limit concentration, or lower, and analyze it after calibration but before any samples are analyzed. The measured concentration of the RLCS should be within a fixed percentage of the true value, such as 50% to 150%. If the results are out of control, repeat calibration and sample determinations since the last acceptable calibration verification. If the sample is being analyzed for regulatory compliance and the fixed percentage is set in regulation or by a USEPA reference method, use that percentage. Otherwise, use the percentage set by the end-user of the laboratory results or by the laboratory.

f. Laboratory blank: The laboratory blank (LB), also known as reagent blank or laboratory reagent blank, consists of reagent-grade distilled or deionized water and any acids or other reagents added to the samples before analysis and analyzed in the same manner as are the other samples. The LB should have a measured concentration of the target element significantly less than the reporting limit, e.g., less than one half of the reporting limit. If samples are being analyzed for regulatory compliance and the percentage is set in regulation or by a USEPA reference method, use that percentage. Otherwise, use the percentage set by the end-user of the laboratory results or by the laboratory. Include a minimum of one LB for every 20 samples in an analytical batch, or include more LBs per batch if appropriate. If the LB exceeds the acceptable concentration, immediately cease sample analysis and initiate corrective action. Corrective action may include recalibrating the instrument if there is instrumental drift or eliminating a source of contamination, such as carryover contamination from samples.

g. Field blank (FB): A field blank is a portion of reagent water placed into a sample bottle and taken out into the field during sample collection. Use the same type of bottle used to collect the samples and treat FB exactly the same as a sample. The FB is used to assess whether analytes or interference could have contaminated the samples during the sampling process. The measured concentration of the FB should be less than a warning level based on the end-user's requirements or set by the laboratory itself, e.g., one-half of the reporting limit (see ¶s 2*e* and *f*, and 3*a*).

h. Laboratory-fortified matrix (LFM)/laboratory-fortified matrix duplicate (LFMD): Use LFM (also known as matrix spike) and LFM duplicate to evaluate the accuracy and precision, respectively, of the method as influenced by a specific matrix. Prepare by adding a known concentration of analytes to the sample in duplicate. The concentration of the fortified samples must be within the LDR. Limit addition volume to 5% or less of sample volume. Ensure that performance criteria for the sample preparation method are satisfied. If the individual method does not specify acceptance criteria, the analyte should be between 70 and 130% of the fortified value and the percent difference between the LFM and the LFMD should be less than 20%. Process fortified samples independently through the entire sample preparation procedure and analytical process. Include a minimum of one LFM/LFMD for every 20 samples in an analytical batch, or include more LFM/LFMDs if appropriate. Additional options for handling LFM results are presented in Section 1020B. If the recovery of the LFM is within acceptance criteria, the sample is considered within control and there is no matrix effect. If the recovery is out of control and the system is demonstrated to be in control, i.e., CCS recoveries are acceptable, then there may be some matrix effect. Additional information on matrix interferences and the Method of Standard Additions is contained in Sections 1020B, 3113B.4*d*2), and the other individual Part 3000 methods. If matrix interference is documented, notify the data-user of this effect.

3. Batch Quality Control

When samples are analyzed directly without any preparation, additional batch quality control is not needed. However, at times,

water samples cannot be analyzed directly and must be treated first, by acid digestion (see Section 3030), for example. When this is done, take additional quality control steps to determine that the sample treatment does not change the composition of the sample.

a. Method blank (MB): A method blank (also known as reagent blank) is a portion of reagent water treated exactly as a sample, including exposure to all equipment, glassware, procedures, and reagents. The MB is used to assess whether analytes or interferences are introduced during sample preparation. The measured concentration of the MB should be less than a warning level based on the end user's requirements or set by the laboratory itself, e.g., one-half of the reporting limit (see ¶s 2*e* and *f*). Include a minimum of one MB with each batch of samples prepared. The MB would replace the LB for samples going through sample preparation.

b. Laboratory-fortified blank (LFB): The laboratory-fortified blank (also known as blank spike) is a method blank that has been fortified with a known concentration of analyte. It is used to evaluate ongoing laboratory performance and analyte recovery in a clean matrix. Prepare fortified concentrations approximating the midpoint of the calibration curve or lower, but well above the RL and MDL. Ensure that the LFB meets performance criteria for the sample preparation method. If the individual method does not specify acceptance criteria, the percent recovery of the LFB should be a fixed percentage of the fortified concentration, for example, 85 to 115%. Establish corrective actions to be taken in the event that LFB does not satisfy acceptance criteria. Include a minimum of one LFB with each batch of samples prepared. Additional options for handling LFB results are presented in Section 1020B.

c. Laboratory-fortified matrix (LFM)/laboratory-fortified matrix duplicate (LFMD): Use LFMs exactly as above (¶ 2*h*) except that the sample should be fortified before sample preparation.

4. References

1. 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. *Federal Register* 5:23703.
2. U.S. Environmental Protection Agency. 1994. Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectroscopy. Method 200.8, rev. 5.4, U.S. Environmental Protection Agency, Cincinnati, Ohio.
3. U.S. Environmental Protection Agency. 1994. Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption. Method 200.9, rev. 2.2, U.S. Environmental Protection Agency, Cincinnati, Ohio.
4. U.S. Environmental Protection Agency. 2001. Trace Elements in Water, Solids, and Biosolids by Inductively Coupled Plasma – Atomic Emission Spectrometry. Method 200.7, rev. 5.0, U.S. Environmental Protection Agency, Washington, D.C.