

CHAPTER 9

Continuing Calibration Verification (CCV)

9-1. Introduction.

Continuing calibration verifications (CCVs) are evaluated to determine whether the instrument was within acceptable calibration throughout period in which samples were analyzed (i.e., to verify that the initial calibration was applicable during the sample analyses). In general, failure of the CCV indicates that the initial calibration is no longer valid and should trigger recalibration and the reanalysis of the associated samples in the analytical sequence.

9-2. Criteria.

9-2.1. Traceability and Reporting Requirements.

The initial calibration and the sample analyses associated with each CCV must be clearly indicated in the run log. The run log must also list the date each CCV standard was analyzed; the time of analysis must also be specified for chromatographic methods. In addition, the source, reference concentration (level spiked), measured concentration, and percent recovery must be reported for each target analyte and surrogate (when surrogates are analyzed). However, for chromatographic methods where the initial calibrations are performed using mean response factors, the **percent differences** for the CCV response factors may be reported instead of percent recoveries (e.g., when the instrument's software cannot readily report CCV recoveries).

9-2.2. Representativeness.

CCVs must be analyzed in the same fashion as other QC samples (e.g., LCSs) and environmental samples (i.e., must be analyzed in a manner that is representative of all other sample in the analytical sequence).

9-2.3. Frequency.

a. All environmental samples in an analytical sequence must be bracketed by (i) an initial calibration and a CCV or (ii) by two CCVs. Therefore, a CCV must be analyzed at the end of every analytical sequence.

b. If replicate CCVs are analyzed in succession before or after a set of samples, the CCVs analyzed *immediately* before and after the samples constitute the bracketing pair of CCVs. For example, "Sample-01" and "Sample-02" are qualified based upon the performance of "CCV-02 and "CCV-03" for the analytical sequence:

CCV-01, CCV-02, Sample-01, Sample-02, CCV-03, CCV-04 ...

c. However, it should be noted that a single reinjection of the CCV is typically performed when a CCV fails. Therefore, if CCV-03 were to fail, the bracketing CCVs would consist of CCV-02 and CCV-04.

9-2.3.1. Chromatographic Methods.

For chromatographic methods, a low-level or mid-level CCV standard must be analyzed at the following frequency: (i) At the *beginning* of the analytical shift/sequence (when an initial calibration is not being performed); (ii) every *12 hours* of analyses or every *10 to 20 samples*, whichever comes first; and (iii) at the *end* of the analytical sequence--*this includes GC/MS methods*.

Note: The term “sample” refers to field samples and batch QC samples such as method blanks, laboratory control samples, matrix spikes, matrix spike duplicates, matrix duplicates.

Note: *Laboratories do not typically analyze a CCV at the end of the run sequence for GC/MS analyses. In order to minimize the occurrence of estimated data, this requirement must be explicitly specified when contracting for laboratory analytical services. Alternatively, a rationale for not analyzing CCVs at the end of the run sequence for GC/MS analyses must be presented in project documents such as the QAPP.*

9-2.3.2. Inorganic Methods.

For inorganic methods, a low-level or mid-level CCV must be analyzed at the following frequency: (i) Every 10 to 15 samples and (ii) at the end of the analytical sequence.

9-2.4. Acceptance Criteria.

The acceptance limits for the CCVs will be highly dependent upon the analytical technique (as well as the end use of the data). Therefore, several assumptions were made to develop the data evaluation strategies that are presented in this section of the document. It was assumed that the acceptance limits for the CCV are more stringent than the acceptance limits for the LCS when the method of analysis involves significant sample preparation and the standards are not fully processed with the environmental samples. Similarly, it was assumed that the CCV and LCS limits will be similar when the method of analysis does not involve significant sample preparation. Lastly, a “gross” CCV failure was typically assumed to occur when a CCV exceeds twice its tolerance for uncertainty.

9-2.4.1. Inorganic Methods.

a. If the method involves significant sample preparation and the CCVs are mid-level standard solutions that are essentially instrument QC samples that are directly analyzed (e.g., CCVs for metals by GF-AA or ICP), then the recovery should be within 90–110%. If the calibration is verified using a CCV set at the low-level calibration standard, then the recovery should fall within 85–115%.

b. Wider acceptance ranges should be used when the CCV is processed in the same manner as the environmental samples (i.e., when the CCV is also an LCS) or when the CCV undergoes a significant preparatory process. For example, CCVs are typically LCSs for the Hg CV-AA analyses. When the CCV is processed in the same manner as the environmental samples, then the CCV should be evaluated using the LCS acceptance limits; an acceptance range of 80–120% should be used. An acceptance range of 85–15% is recommended when the CCV is not processed in an identical manner as the samples but nevertheless undergoes a significant preparatory process (e.g., cyanide CCVs that are distilled but that are not extracted with the environmental samples).

9-2.4.2. Organic Chromatographic Methods.

a. If the calibration is verified with a mid-level CCV, then the recovery should be within 85–115% for analyses of extractable organics (e.g., pesticides and Aroclors). If calibration is verified using a CCV set at the low-level calibration standard, then the recovery should be 80–120%. For purge-and-trap methods (where the environmental samples and CCVs are prepared and analyzed in the same manner), CCVs should be within 20% of their expected values. Wider acceptance ranges may be appropriate for other organic methods where the CCVs are processed in the same manner as the environmental samples.

b. Depending on the analytical method and the level of detail required for the evaluation, additional acceptance criteria may be applicable for chromatographic methods. In particular, for methods that require minimum response factors, the method-specified minimum response factor criteria must be met. Methods such as 8260B and 8270C specify acceptance limits for the responses and retention times of the internal standards in the CCVs. The evaluation of internal standards is discussed in Chapter 16. CCVs are often evaluated to determine if analyte identification criteria are being met. In particular, for chromatographic methods involving the use of two-dimensional detectors (e.g., FIDs and PIDs), CCV retention times are typically assessed to verify that they fall within established retention time windows.

9-3. Evaluation.

a. *Review the instrument run logs to verify that the CCVs were analyzed at an appropriate frequency.* Review the standard preparation log and note whether or not the CCVs and initial calibration standards were prepared from the same source.

b. Use a continuing calibration summary form (and any instrument printouts of quantitation reports) to recalculate a CCV recovery. For chromatographic methods where the initial calibration is performed using mean response factors and **percent differences** are calculated for response factors, calculate the percent difference for at least one response factor. Compare the calculated values with the reported values. The former must agree with the latter to within at least *two* significant figures.

c. “For each CCV, review the CCV summary form to verify that the reported percent recovery or percent difference for each target analyte is acceptable. For chromatographic methods for which minimum response factors are specified, note any response factor that is not compliant with method requirements.

9-4. Qualification.

9-4.1. Representativeness.

a. *Qualify the associated sample results if the CCVs were not analyzed in a representative manner.* In particular, the number of replicate analyses and system “clean-out” activities must not be applied to CCVs to a greater extent than to the environmental samples in the analytical sequence.

b. If the *run sequence log* indicates that multiple CCBs (continuing calibration blanks) are analyzed before the CCVs but not before any of the environmental samples, then the CCVs may not be representative. If the replicate CCB analyses were being performed to address “carry over”, then qualify the associated sample results as estimated or rejected depending upon the severity of the blank contamination and the intended use of the data. Ideally, the laboratory should be required to provide the entire raw data package and the CCB with the highest level of “carry over” (typically the first CCB in the run sequence) should be used to qualify the associated sample results for blank contamination using the strategies in Chapter 10. However, when the CCB results are not available, at a minimum, qualify all detections in the associated environmental samples as estimated (with the J+ flag).

c. If multiple CCVs are being analyzed, the representativeness of the CCV results must be critically evaluated. For example, assume that the following run sequence is observed for a set of aqueous VOC analyses:

CCV-01, CCV-02, CCV-03, CCV-04, Sample-01, Sample-02, MB, CCV-05, CCV-06,
CCV-07 ...

d. Assume that CCV-04 and CCV-07 are acceptable (i.e., the CCV recoveries fall within the acceptance range), but the remaining CCVs are unacceptable. Although two acceptable CCVs bracket the samples, the run sequence suggests that the CCVs are not being analyzed in an appropriate (i.e., representative) manner. When analytical problems exist (especially when a method is only marginally out-of-control), if a sufficient number of QC samples (such as CCVs) are analyzed, then one of the QC samples will eventually fall within the acceptance limits by chance (i.e., because of random error)! Method performance appears to be acceptable but is actually substandard (most of the CCVs are not falling within the acceptance limits). Under these circumstances, qualify the associated sample results (e.g., Sample-01 and Sample-02) using the most noncompliant CCV recovery. If this information is not available (e.g., the recoveries for only CCV-04 and CCV-07 are reported), then qualify all the associated sample results for marginal CCV failure (refer to Chapter 9-4.4). If the data are being used to support critical decisions, it may be appropriate to qualify the sample results as tentatively unusable (using the X flag).

c. CCVs are occasionally used to “update” the instrument’s calibration data (e.g., “resloping” for GF-AA analyses). This is not the objective of a CCV. A CCV is performed to verify (to within some tolerance for uncertainty) that the initial calibration remains valid and is not performed to alter the initial calibration curve. “Updating” the calibration using the CCV primarily amounts to replacing the original multiple-point calibration with a single-point calibration. When this occurs, recalculate the associated results using the original calibration curve or, at a minimum, qualify the results as estimated. However, professional judgement should be used. For example, when there is significant instrumental drift and a calibration line is updated using the CCV, results calculated from the CCV (particularly mid-range detections) may be more accurate than those calculated from the multiple-point calibration!

9-4.2. Frequency.

a. If a CCV is missing at the end of the analytical sequence, then, at a minimum, qualify all detections with the J flag and all nondetections with the UN flag *unless it can be otherwise demonstrated that the instrument remained in calibration for the entire analytical sequence*. For example, the laboratory may have analyzed extremely “dirty” environmental samples near the end of the run sequence and cleaned the instrument to eliminate “carry over” problems only for the next 12-hour CCV. Qualification of the associated sample results with the X flag may be more appropriate for some data uses (e.g., when the data is being used to support critical decisions).

b. If all samples are bracketed by two acceptable CCVs but the CCVs are not analyzed at the appropriate frequency (e.g., after every 10 to 20 samples), use professional judgement to determine whether data qualification is necessary. For significant nonconformances, qualify detections with a J flag and nondetections with the UN flag.

9-4.3. Tolerance for Uncertainty.

a. In general, if a CCV in an analytical sequence is not acceptable, then qualification is required for all samples following the last acceptable CCV and all samples preceding the next acceptable CCV. For example, consider the following run sequence:

CCV-01, Sample-01, Sample-02, CCV-02, Sample-03, Sample-04, CCV-03, Sample-05, Sample-06, CCV-04 . . .

b. “Sample-01” to “Sample-04” would be qualified if CCV-02 were unacceptable. Qualification protocols for CCV failures are very similar to those for LCS failures. Marginal CCV failures are distinguished from gross failures as discussed below.

9-4.3.1. Inorganic Methods, CCVs Not Processed with Samples.

If the CCV does not undergo a significant preparatory process relative to the environmental samples, then evaluate the CCV results as follows: If the CCV recovery is unacceptable but falls within 80% to 120%, then qualify the data (i.e., the associated sample results) for *marginal* failure. If the CCV recovery is unacceptable and does not fall within 80% to 120%, then qualify the data for *gross* failure.

9-4.3.2. Inorganic Methods, CCVs Processed with Samples.

If the CCV is processed in the same manner as the environmental samples, then the CCV is essentially an LCS and must be evaluated using the LCS limits. The results should be qualified for *marginal* failure if the CCV is unacceptable but falls within 60% - 140% of the expected value. If the CCV undergoes a significant sample preparatory process but is not processed in an identical manner as the environmental samples, then it is recommended that results be qualified for marginal failure if the CCV is unacceptable but falls within 70% - 130% (e.g., cyanide CCVs that are distilled but not extracted with the environmental samples).

9-4.3.3. Organic Methods, CCVs Not Processed with Samples.

The following guidance applies to methods that require significant sample preparation (e.g., solvent extractions or cleanup procedures) and the CCV is not processed with the environmental samples. If the CCV is unacceptable but the percent recovery falls within 70% to 130% or the percent difference for the response factor is not greater than 30%, then qualify the data for *marginal* failure. If the CCV is unacceptable and the percent recovery does not fall within 70% to 130% or the difference for the response factor is greater than 30%, qualify the associated sample results for *gross* failure.

9.4.3.4. Organic Methods, CCVs Processed with Samples

If the method does not require significant sample preparation or the CCV is processed with the samples (e.g., aqueous purge-and-trap analyses), the CCV is unacceptable but the percent recovery falls within 40% to 160% or the percent difference for the response factor is not greater than 60%, then qualify the data for *marginal* failure. If the CCV is unacceptable and the percent recovery does not fall within 40% to 160% or the difference for the response factor is greater than 60%, then qualify the associated sample results for *gross* failure.

9.4.4. General Qualification Strategies.

a. Environmental sample results are qualified for CCV failure, based upon the (i) direction of bias, (ii) the magnitude of the failure, and (iii) the concentration of the target analyte relative to the AL. The direction of bias for a CCV failure is *well defined* when all other associated QC samples (e.g., ICVs and LCSs) are in control or exhibit bias in the same direction, i.e., if the CCV recovery is unacceptably high but the LCS recovery is unacceptably low, then the direction of bias is not well defined. Similarly, if the ICV is unacceptable or if a second source standard was used to prepare the CCV and the CCV is unacceptable, then the direction of bias cannot be inferred from the CCV recovery. Qualification strategies for CCV failures follow.

(1) If the CCV is *marginally* unacceptable and the direction of bias is *well defined*, then the data is qualified as follows: For *low* bias, qualify detections with the J- flag and nondetections with the UN flag. For *high* bias, qualify detections with the J+ flag and nondetections with the U flag.

(2) If the CCV is *marginally* unacceptable and the direction of bias is *not* well defined, then qualify detections with the J flag and nondetections with the UN flag.

(3) If the CCV is *grossly* unacceptable and the direction of bias is *well defined*, then qualify the associated sample results as follows:

(a) For *low* bias, qualify all nondetections with the R flag. When an AL is *not* specified, qualify detections with the J- flag. If an AL is specified, then qualify detections less than the AL with the X flag and qualify detections greater than the AL with the J- flag.

(b) For *high* bias, qualify all nondetections with the U flag. Qualify detections with the J+ flag. However, when an AL is specified, it may be appropriate to qualify detections greater than the AL with the X flag. Alternatively, it may be desirable to obtain additional information from the laboratory before completing the evaluation. For example, additional data could be requested to determine if the high CCV recovery resulted from “carry over” or improper integrations

(4) If the CCV is *grossly* unacceptable and the direction of bias is *not* well defined, then qualify nondetections with the R flag. When an AL is *not* specified, qualify detections with the J flag. If an AL is specified, qualify detections with the X flag. (However, if possible and practical, the magnitude of the uncertainty relative to the proximity of the detection to the AL should be taken into account.)

b. The qualification strategies discussed above are illustrated in Table 9-1 (where it is assumed that each CCV must be within 10% of its expected values). *However, CCV failures must be interpreted in the context of other instrumental and batch QC results using professional judgement.* In particular, a result may still be acceptable when an associated CCV does not fall within the CCV acceptance limits because the uncertainty tolerance for instrumental performance is typically more stringent than that for overall method performance. For example, if the CCV recovery must be within 10% of its expected value and the LCS must be within 20% of its expected value, but the CCV recovery is 85% and the LCS recovery is 80%, then overall accuracy of the associated sample results is still acceptable. In general, if the direction of bias is well defined and the LCS is in control, sample qualification is not required when the CCV recovery is marginally unacceptable. (However, under these circumstances contractual corrective action may be appropriate.)

Table 9-1
Data Qualification for CCV Results ¹

%R for CCV Bias	Remarks	Sample (y)	Flag
90% ≤ %R ≤ 110%	Acceptable %R	MRL < MQL < y	None
		MRL < y < MQL	J
		y < MRL	U
110% ≤ %R ≤ 120% or 80% ≤ %R ≤ 90% Undefined Bias	Marginal Failure	y > MRL	J
		y < MRL	UN
80% ≤ %R ≤ 90% Low Bias	Marginal Failure	y > MRL	J-
		y < MRL	UN
110% ≤ %R ≤ 120% High Bias	Marginal Failure	y > MRL	J+
		y < MRL	U
%R < 80% Low Bias	Gross Failure	y > MRL	X if y < AL J- otherwise
		y < MRL	R
%R > 120% High Bias	Gross Failure	y > MRL	J+ Possibly, X if y > AL
		y < MRL	U
%R > 120 or %R < 80% Undefined Bias	Gross Failure	y > MRL	J if AL not specified; X if AL specified
		y < MRL	R

Notes: 1. %R, MRL, MQL, AL, and y denote the percent recovery of the target analyte in the CCV, method reporting limit, method quantitation limit, AL, and concentration of the target analyte in an associated field sample, respectively. It is assumed that the MRL is greater than the MDL, less than the MQL, and less than the AL.