

## CHAPTER 11

### Laboratory Control Samples (LCSs)

#### 11-1. Introduction.

**Laboratory control samples** are evaluated to assess overall method performance and are the primary indicators of laboratory performance. In general, laboratory control samples are similar in composition as the environmental samples, contain known concentrations of *all* the analytes of interest, and undergo the same preparatory and determinative procedures as the environmental samples. LCS recoveries are used to measure accuracy. The relative percent difference (RPD) for duplicate LCS recoveries is normally used as a measure of precision. When both a laboratory control sample (LCS) and laboratory control sample duplicate (LCSD) are processed for a batch of samples, there is no significant physical distinction between the LCS and LCSD. *Both the LCS and LCSD must satisfy the same recovery acceptance criteria.* Therefore, for simplicity, the term *LCS* will refer to one or more laboratory control samples (e.g., the term “LCS acceptance criteria” will refer to the acceptance criteria for both the LCS and LCSD).

#### 11-2. Criteria.

##### 11-2.1. Frequency.

*At least one LCS must be reported with each batch of samples.* A laboratory control sample and a laboratory control sample duplicate (LCSD) may be analyzed to provide information on the precision of the analytical method. The generation of control chart limits for precision via the analysis of LCS/LCSD pairs is an effective means to measure method precision. Multiple LCSs may be required to evaluate method precision and accuracy at different spiking concentrations.

##### 11-2.2. Acceptance Limits.

*a.* Project documents such as the QAPP should specify the acceptance limits for LCS recoveries. To the extent possible, LCS acceptance limits should be established based upon project DQOs rather than upon contractual specifications, the limitations of the laboratory, or the limitations of the analytical method. Laboratory statistical control limits should be evaluated during the planning stages of the DQO process to assure that project-required acceptance limits will be met.

*b.* *Laboratory statistical control limits must not be the sole basis upon which project-required acceptance limits are established.* Statistical control limits generated by the laboratory may be representative of routine method performance but may be too wide to satisfy project-specific DQOs. Furthermore, statistical control limits for laboratory control samples tend to adversely impact laboratory-to-laboratory comparisons (e.g., when USACE QA split sample analyses are being performed, an LCS recovery that falls within the wide acceptance range of one laboratory will not necessarily fall within the tighter acceptance range of the referee laboratory or vice versa).

c. Acceptance limits for bias and precision are presented in various analytical methods (e.g., SW-846 and CLP methods) but *many of these limits may be inappropriately wide*. Acceptance limits for accuracy and precision are presented in the USACE Shell. Although these limits were established to ensure a moderate to high level of data quality, they are ultimately contractual in nature (e.g., permit poor performance for select target analytes because of inherent limitations of the analytical methodology). It may not be practical or possible (even after method modification and development) for a method to routinely meet the acceptance limits for every target analyte. Under these circumstances, the reviewer must distinguish contractual compliance and laboratory performance issues from data usability issues.

d. Inappropriately wide LCS acceptance ranges may be specified for a method in project-documents such QAPPs, SAPs, and Work Plans. These acceptance ranges are often based upon contractual, method-specified, or laboratory control chart limits. For example, erroneously wide LCS acceptance ranges may be specified when ALs are equal to or near the MQLs. *The specification of an acceptance limit in a project document per se does not imply that limit is scientifically sound with respect to project objectives. When, in the reviewer's professional judgment, project-specified LCS acceptance limits are not consistent with project DQOs, evaluate the data package with respect to scientifically defensible limits.*

e. In the absence of reasonable LCS recovery limits, the following limits are recommended: The recovery for each target analyte should fall within 80 to 120% for *inorganic* analyses and within 60 to 140% for *organic* analyses. For *purge-and-trap* GC and GC/MS analyses, recoveries should fall within 80% to 120% when the CCV is being used as the LCS. If the LCS is an independent source standard, the LCS should fall with 70 to 130% for *purge-and-trap* analyses.

f. In the absence of project-specific limits for precision, it is recommended that the acceptance limit for the RPD be equal to one half of the width of the corresponding LCS recovery acceptance range or to the laboratory's RPD acceptance limit, whichever is less. For example, the laboratory may have established statistical RPD acceptance limits by processing an LCS/LCSD pair for each batch or from interbatch LCSs (i.e., LCSs from consecutive batches).

### 11-3. Evaluation.

Evaluate the LCS results using the following strategies:

a. Using the standard preparation logs verify that *all* target analytes were spiked into the LCS and note whether or not an independent-source standard was used to prepare the LCS.

Note: A number of published analytical methods do not require the LCS to contain all the target analytes. Unless a scientifically defensible rationale for not spiking all the target analytes is presented in the analytical method or in project documents such as the QAPP, assume that all "single-component" target analytes must be spiked into the LCS. However, when several multi component target analytes are being simultaneously analyzed (e.g., the set of Aroclors in Method 8082), it may not be possible (or desirable) to spike all the analytes into a single LCS. Depending on the nature of the analysis and

the data quality objectives for the project, a set of laboratory control samples (e.g., one LCS for each multi component target analyte) may be required or only a single LCS containing “representative” components may be appropriate (e.g., an LCS containing Aroclors 1016 and 1260 is typically assumed to be representative of the other Aroclors analyzed by Method 8082).

*b.* Using the sample preparation log and the instrument run log verify that the LCS was processed with the samples through the entire analytical method.

*c.* Using the LCS summary form, calculate the LCS recovery for at least one target analyte and compare the calculated value to the reported value. Similarly, recalculate the RPD for an LCS/LCSD pair for one target analyte and compare the calculated value to the reported value. The calculated LCS recoveries and RPDs must agree with the reported values to within two significant figures.

*d.* For each target analyte, compare the LCS recoveries and RPDs reported on the laboratory’s summary forms to the corresponding LCS acceptance limits for bias and precision. In the absence of appropriate acceptance limits, establish a set of limits to properly evaluate the LCS results. A batch of samples is acceptable only for those target analytes that satisfy the LCS criteria for bias and precision. All failures must be noted. Data qualification is required when the LCS acceptance criteria are not met.

*e.* Review the Case Narrative and note any problems discussed for the LCS. When an LCS recovery is unacceptable, examine the Case Narrative and note why the batch was not reprocessed (e.g., reextracted and reanalyzed) for the failed analyte. However, it should be noted that even when method implementation is optimal, a small percentage of sporadic failures should be expected for the LCS (especially when a large number of target analytes are being simultaneously analyzed).

#### **11-4. Contractual Considerations.**

*a.* Contractual considerations may impact the data review. Since laboratories are normally required to reprocess (e.g., reextract and reanalyze) a batch of samples when the LCS is unacceptable, contractual corrective action for unsatisfactorily performance is typically required for gross systematic LCS failures. When gross systematic failures occur, the reviewer should consult with the Project Manager to determine whether or not to proceed with the review or to reject the data package as a whole (e.g., the laboratory may be required to reanalyze the environmental samples). However, the reviewer should exercise professional judgment when determining whether contractual compliance will impact the data review. In particular, for methods containing large lists of target analytes (e.g., Method 8270C) or “poor performers” (e.g., the ketones of Method 8260B or other analytes which cannot meet QC limits because of inherent method limitations), it is highly probable that the recoveries of several target analytes will be unacceptable.

*b.* *Sporadic marginal LCS failures should be expected and should not trigger a consultation with the Project Manager or the rejection of a batch of samples.* For example, a “marginal

sporadic failure” may be said to exist if an LCS recovery falls between the three- and four-sigma control limits for no apparent reason for a particular batch of samples but the laboratory control samples for prior and subsequent batches are acceptably recovered. The table below lists the maximum number analytes expected to fall outside of the three-sigma control limits for an LCS when the LCS contains a large set of target analytes..

c. For example, according to Table 11-1, if there are 20 target analytes, as many as two analytes in the LCS may fall outside of the three-sigma acceptance limits because of random error. Typically, these types of sporadic failures should not trigger reanalyses of the batch but the associated environmental sample results should be qualified.

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**Table 11-1**  
**Number of Target Analytes Versus Number of Expected LCS Failures**

$n^1$	$f^2$
10–15	1
16–45	2
46–85	3
86–130	4

Notes: 1.  $n$  = Total number of target analytes being simultaneously analyzed. 2.  $f$  = Maximum number of analytes expected to fall outside of the three-sigma control limits with 99% confidence if the probability of a random failure is less than or equal to 1%.

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Note: Review project documents (e.g., the Quality Assurance Plan) to ensure that the noncompliant analyte is not a critical analyte (e.g., a human or ecological “risk driver”). For example, if 60 VOCs are being analyzed by 8260B, but vinyl chloride is the primary contaminant of concern, then reanalyses for vinyl chloride should be expected when the LCS recovery is not acceptable.

d. If precision is unacceptable for a particular analyte (e.g., the RPD is higher than the acceptance limit), then the associated field sample detections above the MQL (or the MRL if it is greater than the MQL) must be qualified as estimated data. To satisfy project-specific requirements, the laboratory may be required to reprocess a batch of samples when the LCS does not satisfy precision acceptance criteria. Under these circumstance, verify that this was done. However, it should be noted that laboratories do not typically reprocess environmental samples for unacceptable RPDs when the LCS recoveries are acceptable.

#### **11-5. Qualification.**

a. The qualification strategies presented in this section of the document will generally be applicable.

(1) When multiple laboratory control samples (e.g., an LCS and LCSD) are processed for a single batch of samples, and one or more LCS recoveries are unacceptable for a particular target, then the associated samples must be qualified on the basis of the most noncompliant target analyte recovery. However, it should be noted that replicate laboratory control samples may not be required or reported. For example, if the RPD for an LCS/LCSD pair is calculated using interbatch laboratory control data (i.e., the LCSD is not extracted with the LCS but is the control sample for a consecutive batch of samples), the LCSD recovery may not have been reported..

(2) Data qualification must be a function of both the magnitude and direction of the QC failure. *Gross* QC failures must be distinguished from *marginal* failures and the direction of bias must be taken into account. When the LCS recovery is unacceptable, the direction of bias will be said to be *well defined* if the direction of bias for other batch and **instrument QC samples** (e.g., ICVs, surrogates, and replicate LCSs) is consistent with the noncompliant LCS recovery. For example, if both an LCS and LCSD are extracted with a batch of samples and the LCS recovery is less than the lower control limit but the LCSD recovery is greater than the upper control limit, then the direction of bias is not well defined. Similarly, the direction of bias is not well defined when the RPD for an LCS/LCSD pair is used to evaluate duplicate precision and the RPD is unacceptable, but the LCSD recovery is not reported

*b.* Specific qualification protocols for laboratory control samples are presented below and are illustrated in Table 11-2 (where it is assumed that all QC samples other than the LCSs are in control).

(1) If the LCS recovery is *marginally* unacceptable and the direction of bias is *not* well defined, then qualify detections of the target analyte with the J flag and nondetections with the UN flag.

(2) If an LCS recovery is *marginally* unacceptable and the direction of bias is *well defined*, then qualify the data 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.

(3) If an LCS recovery 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. If 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 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 (e.g., when a conservative estimate is not being sought).

(4) If the LCS recovery is *grossly* unacceptable and the direction of bias is *not* well defined, then qualify nondetections with the R flag. If an AL is *not* specified, then, at a minimum,

qualify detections with the J flag (the X flag may be more appropriate). If an AL is specified, qualify detections less than the AL with the X flag. Depending on project DQOs, qualify detections greater than the AL with the J or X flag.

c. In addition to the qualification strategies discussed above, use the following protocols when duplicate laboratory control samples are processed with each batch of samples:

(1) If the LCS/LCSD recoveries are acceptable, the RPD 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.

(2) If the RPD is *grossly* unacceptable and the direction of bias is *not* well defined, then qualify nondetections with the R flag. (The X flag may be appropriate if additional information to determine the direction of bias will be obtained). Qualify detections with the J flag when an AL is *not* specified. 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 or the X flag.

d. In the absence of valid project-specific limits for bias and precision, a *gross* failure is defined to occur when one of the following conditions is satisfied:

(1) For *inorganic* analyses, a gross failure occurs for a target analyte when the percent recovery does not fall within 60 to 140%. For *organic* analyses involving *significant sample preparation* (e.g., solvent extraction), a gross failure occurs when the LCS recovery does not fall within 20 to 180%. However, for *purge-and-trap* analyses, a gross failure occurs when the LCS recovery does not fall within 40 to 160%.

(2) A *gross failure* occurs when the RPD for the LCS/LCSD is greater than 40% for *inorganic* analyses, 60% for *purge-and-trap* analyses, and 80% for *extractable organic* analyses.

## 11-6. Qualification Strategies Using Estimates of the Uncertainty.

a. This section of the document describes some optional data qualification strategies that may be used when analytical uncertainty can be estimated from laboratory control samples. These strategies will be applicable when matrix interference and sample heterogeneity are not significant components of the analytical uncertainty or when it is desirable to establish a *lower bound* for the total uncertainty. Laboratory uncertainty is estimated from the laboratory's in-house statistical warning and control limits for LCS recoveries. If representative matrix spike warning and control limits are available, it is recommended that these limits be used instead of the LCS limits. The use of matrix spike warning and control will result in better estimates of the uncertainty (e.g., since LCS limits do not account for the uncertainty associated with matrix effects). However, it should be noted that representative matrix spike recovery limits are not typically available from environmental production laboratories and must be generated on a project-specific basis. (Refer to Chapter 12 for additional information.)

b. When an analytical result is being compared to a decision limit, it may be useful (e.g., for the purposes of data qualification) to estimate an upper or lower confidence limit for the re-

sult. If there is significant analytical bias (i.e., the percent recovery for the LCS is statistically different from 100%), the result can be corrected for bias prior to estimating confidence limits. Since low bias is more common than high bias for environmental analyses (e.g., for extractable organic compounds) and is more likely to adversely impact data quality than high bias, only low bias will be addressed. Upper confidence limits (UCLs) will be approximated by correcting for low bias and taking random error into account. The upper confidence limits will then be compared to project action levels to qualify results. This strategy will constitute a relatively conservative approach for risk-based applications.

*c.* If the percent recovery of a target analyte in the associated LCS is not too close to zero (e.g., the percent recovery is least 20–30%), precision is in control, then an upper confidence limit for a laboratory result may be approximated using the following equation<sup>1</sup>:

$$\text{UCL}(C, \%R, \alpha) = u(C, \%R, \alpha) [ C / (\%R / 100) ] \quad (11-1)$$

*d.* The measured concentration of the sample and percent recovery for the associated laboratory control sample are denoted by  $C$  and  $\%R$ , respectively. The second term in Equation 11-1 (enclosed in brackets) is the “biased corrected concentration.” The first term,  $u(C, \%R, \alpha)$ , will be referred to as the “uncertainty factor” because it accounts for the random error associated with the measured result  $C$  and the calculated percent recovery  $\%R$ . The factor is primarily a function of  $C$ ,  $\%R$ , and the desired level of statistical confidence,  $\alpha$ . The factor will be some positive value greater than one. The use of a high value for the uncertainty factor will result in a conservative estimate for the UCL (e.g., will minimize false negatives when comparing results to an AL).

*e.* If normality is assumed and the relative uncertainty (i.e., the relative standard deviation) is assumed to be constant within the quantitation range of the method, then the “uncertainty factor” for the 95% UCL may be estimated using the following equation:<sup>2</sup>

$$u(95\%) \approx 1 + (2)^{1/2} (L_{95\%} / \%R) \quad (11-2)$$

where  $L_{95\%}$  is half the width of the warning range for the LCS percent recoveries (e.g., from the laboratory’s control charts). The half width of the control range,  $L_{99\%}$ , gives an upper 99% upper confidence limit.

$$u(99\%) \approx 1 + (2)^{1/2} (L_{99\%} / \%R) \quad (11-3)$$

Note that the uncertainty increases as the width of the warning or control ranges increases and the percent recovery decreases.

<sup>1</sup>For a rigorous treatment of propagation of analytical measurement uncertainty, refer to the following reference: “Draft EURACHEM/CITAC Guide Quantifying Uncertainty in Analytical Measurement,” Second Edition, June 1999, EURACHEM Measurement Uncertainty Working Group.

<sup>2</sup>Georgian, T. Estimation of laboratory uncertainty using laboratory control samples. “Environmental Testing and Analysis,” Vol. 9, No. 6, p. 20. November/December 2000.

f. The assumption that the relative standard deviation is constant will be valid for sample concentrations sufficiently near the spiking concentration for the LCS (typically the mid-calibration range) and will be appropriate when the standard deviation is approximately a linear (increasing) function of concentration. Uncertainty is often proportional to analyte concentration when the measurements are well above the detection limits. The above equations will probably result in reasonable estimates when there is no appreciable matrix interference or sample heterogeneity, measurements are within the calibration range of the method, and the analyte levels are near the LCS spiking concentration. Note that the variability associated with the heterogeneity of the sample matrix is not taken into account because the total uncertainty is estimated from the LCS, which is typically a “clean” matrix such as reagent water or purified sand.

g. The use of the mean LCS recovery (%R), rather than the use of a single LCS recovery, %R, associated with a batch of samples, will generally result in a more reliable estimate of the UCL. This is especially true when extreme low bias (e.g., %R < 20% or 30%) or high method variability exists. Under these circumstances, bias correction should be performed using the mean percent recovery. If the mean LCS recovery is available (e.g., at least 20 or 30 data points were used to establish the laboratory’s in-house statistical warning and control limits) *and the method is in statistical control*, then substitute (<%R>) for %R in Equation 11-1 and use the following uncertainty factors:

$$u(95\%) \approx 1 + (L_{95\%}/\langle\%R\rangle) \quad (11-4)$$

$$u(99\%) \approx 1 + (L_{99\%}/\langle\%R\rangle) \quad (11-5)$$

h. Note that (when bias correction is performed) the use of the mean recovery decreases the uncertainty (and the UCL) because the mean recovery is a more confident representation of “true” bias than any single recovery value.

i. If there is no significant bias (i.e., %R = 100%), the relative uncertainty is approximately constant within the quantitative range of the method and the associated LCS recovery is in control for the sample batch, then Equation 11-1 and either Equation 11-4 or Equation 11.5 may be used to estimate an upper confidence limit, by setting <%R> = 100:

$$UCL(95\%) = u(95\%) C \approx (1 + L_{95\%}/100) C \quad (11-6)$$

$$UCL(99\%) = u(99\%) C \approx (1 + L_{99\%}/100) C \quad (11-7)$$

j. Note that the total uncertainty is larger when a bias correction is performed. This occurs because Equation 11-1 contains two sources of uncertainty (the uncertainty associated with %R and C) while Equations 11-6 and 11-7 contain only one source of uncertainty (uncertainty associated with C).

k. To illustrate the use of the above equations, assume that %R = 40% and C = 2 ppb. If the LCS warning range is 60–140%, then  $L_{95\%} = 40\%$ . It follows from Equations 11-1 and 11-2 that the upper confidence limit for the measured result C is:

$$\text{UCL}(95\%) = (1 + 1.4) [ 2 \text{ ppb} / (40\% / 100) ] \approx 12 \text{ ppb}$$

*l.* If there is no significant method bias and the LCS recovery is in control, then the upper confidence limit can be estimated using Equation 11-1 and Equation 11-6:

$$\text{UCL}(95\%) = 1.4 (2 \text{ ppb}) \approx 3 \text{ ppb}$$

*m.* Once an upper confidence limit is calculated, the upper confidence limits can be compared to the project decision limits and this information can be used to qualify the data. To illustrate, let %R = 40%, C = 2, and  $L_{95\%} = 40\%$  (the first example presented above). Assume that the project-required acceptance range for the LCS is 80–120% and the project action level (AL) is 50 ppb. Since the LCS recovery is 40%, the result C = 2 must be qualified (e.g., as estimated or rejected). Since  $\text{UCL}(95\%) = 12 \text{ ppb} < \text{AL} = 50 \text{ ppb}$ , despite the low bias, it is not likely that the analyte is actually present in the sample at a concentration that exceeds the AL. Hence, it would be appropriate to qualify the 2-ppb result with the J-, flag. However, if AL = 5 ppb, since the  $\text{UCL} > \text{AL}$ , it may be more appropriate to qualify the result with the X flag (e.g., when statistical analyses are not being performed and each reported sample concentration is being directly compared to the AL). The low-biased result of 2 ppb does not demonstrate that the analyte is present at a level that is less than the 5-ppb action level

*n.* It should be noted that the uncertainty factor does not typically exhibit a large amount of variability in the context of the tolerances normally applied to laboratory environmental analyses. The uncertainty factor will typically assume values between two to four, and, at worst, will probably be less than ten. For example, if %R = 20% and the LCS control range is 20% to 180%, conditions that are indicative of rather poor method performance for a target analyte, then an uncertainty factor of less than seven would be calculated from Equation 11-3. Therefore, if the LCS recovery is unacceptably low but the recovery is not less than about 20%, then it may be more convenient to calculate an UCL for a measured sample concentration by correcting the measured concentration for bias and then simply multiplying the bias-corrected result by a factor of five or ten. The UCL could then be compared to the AL to qualify a sample result associated with the noncompliant LCS recovery. For example, if the UCL were less than the action, then the result would be qualified as estimated (e.g., using the J- flag). If the UCL were greater than the AL, then the sample result would be qualified potentially rejected (using the X flag).

**Table 11-2**  
**Data Qualification for LCS Results <sup>1</sup>**

<b>Acceptance Criteria: <math>80\% \leq \%R \leq 120\%</math>, <math>RPD \leq 20\%</math></b>			
<b>%R [RPD]</b>	<b>Remarks [Bias]</b>	<b>Sample (y)</b>	<b>Sample Flag</b>
90% [18%]	%R and RPD in control	MRL < MQL < y	Flag not required.
		MRL < y < MQL	J
		y < MRL	U
90% [30%]	%R acceptable RPD OFC [Unknown]	y > MRL	J
		y < MRL	UN
70% [15%]	%R < LCL [Low]	y > MRL	J-
		y < MRL	UN
140% [10%]	%R > UCL [High]	y > MRL	J+
		y < MRL	U
10% [15%]	%R << LCL [Low]	y > MRL	J- X if y < AL
		y < MRL	R
250% [20%]	%R >> UCL [High]	y > MRL	J+ Possibly X if y > AL
		y < MRL	U
250% [200%] or 10% [200%]	%R >> UCL or %R << LCL RPD grossly OFC [Unknown]	y > MRL	J X if y < AL Possibly X if y > AL
		y < MRL	R

Notes: 1. %R and RPD denote the percent recovery for the LCS and the relative percent difference for the LCS/LCSD, respectively. The concentration of the field sample is denoted by y and the action level by AL. (It is assumed that MRL < AL.) The terms “out of control,” “upper control limit,” and “lower control limit” are abbreviated as OFC, UCL, and LCL, respectively. The inferred direction of bias is enclosed in brackets. The symbols “<<” and “>>” denote “much less than” and “much greater than,” respectively.