

## CHAPTER 13

### Surrogates

#### 13-1. Introduction.

Surrogates are organic compounds that are similar in chemical composition to the analytes of interest and spiked into environmental and batch QC samples *prior* to sample preparation and analysis. Surrogate recoveries for environmental samples are used to evaluate matrix interference on a sample-specific basis. However, in order for this approach to be viable, the surrogates must behave in the same manner as the corresponding target analytes that are native to the matrices of interest (e.g., must partition between various phases in the same manner as the native target analytes). Unfortunately, in practice, this equivalency is typically difficult to demonstrate and is often more assumed than empirically derived. The most representative surrogate will typically be an isotopically-modified version of the target analyte. Therefore, when evaluating surrogate results, the representativeness of the surrogates should always be taken into account.

#### 13-2. Criteria.

*a. The acceptance for surrogate recoveries must take the end use of the data into account and must not be based solely upon contractual or method-specified limits. Method-specified surrogate acceptance limits (e.g., for SW-846 and CLP methods) are often inappropriately wide. Statistically-based acceptance limits generated by the laboratory may be representative of routine method performance but may also be too wide (i.e., may not satisfy project-specific DQOs).*

*b. The acceptance ranges for surrogate and target analyte spike recoveries must be similar (particularly for laboratory control samples and blanks), since, by definition, surrogates and target analytes are chemically similar compounds.*

Note: It is common for statistical control limits for surrogates to be significantly wider than the control limits for target analytes. This often occurs when surrogate control limits are calculated by inappropriately grouping surrogate recoveries from LCSs, MSs, and environmental samples into a single data set.

*c. When the surrogate acceptance ranges are significantly wider than the acceptance ranges for the target analyte, then the appropriateness of the surrogate acceptance ranges must be carefully evaluated prior to performing data review or validation. When the surrogate acceptance limits are inappropriately wide, establish “default” acceptance limits using the target analyte acceptance ranges if these ranges appear to be reasonable. For example, if the acceptance ranges for the target analytes are approximately 70–130% (e.g., for the LCS) and the surrogate acceptance limits are 20–150%, set the acceptance range for the surrogates to 70–130%. Otherwise (i.e., in the absence of more appropriate acceptance limits), surrogate recoveries for organic methods should be evaluated using the acceptance ranges of 80–120% for purge-and-trap methods and 60–140% for extractable organic methods. However, if the LCS is prepared from an independent-source standard, then an acceptance range of 70–130% may be used for purge-and-trap methods.*

*d.* If an analytical method requires *no more than two surrogates*, then surrogate results are acceptable only if *all* of the surrogate recoveries are in control. If three or more surrogates are associated with a set of target analytes, then one surrogate may be marginally (but not grossly) out of control. However, the marginal failure must not be systematic in nature (i.e., must occur in a sporadic or random manner). In particular, if several consecutive failures are observed for the same surrogate, then the data must be qualified.

### **13-3. Evaluation.**

Review the laboratory Case Narrative and the summary forms and note any surrogate failures that are reported. A significant amount of professional judgement is required to evaluate surrogate results. However, the following strategies are generally applicable:

*a.* Prior to reviewing the surrogate data, examine the Case Narrative to determine whether any of the surrogate results should *not* be used to qualify the environmental sample results.

(1) Do not qualify environmental samples for matrix interference when surrogate recoveries are unacceptable because of localized chromatographic problems. For example, if several surrogates are associated with a group of target analytes and some (but not all) of the surrogate recoveries are unacceptable because of coeluting interferences, then qualification is not required.

(2) Do not qualify environmental samples for matrix interference when surrogate recoveries are unacceptable because of dilutions. For example, if all of the surrogate recoveries for an environmental sample are unacceptable because the surrogates were “diluted out,” but the surrogate recoveries for the LCS and associated blanks are acceptable, then no further action is typically required.

(3) It is recommended that the raw data be requested for review when zero-percent surrogate recoveries are reported and these recoveries are not attributed to dilution. Zero-percent recoveries may arise from retention time shifts rather than from losses (e.g., during extraction).

*b.* If an unacceptable surrogate recovery is associated with only a subset of the target analytes (e.g., the surrogate is representative of the performance for only the acid fraction of the BNAs analyzed by Method 8270B), then qualify the results for only the subset of analytes.

*c.* Surrogate recoveries for laboratory control samples and method blanks characterize overall laboratory method performance in the absence of matrix interference are evaluated in much the same manner as target analyte recoveries. Distinguish unacceptable surrogate recoveries arising from matrix effects beyond the control of the laboratory from failures arising from poor laboratory analytical technique. When a surrogate recovery is out-of-control for an environmental sample but is also out-of-control for the LCS or an associated blank (e.g., the method blank), a laboratory performance problem rather than a matrix effect must be assumed.

*d.* Check for transcription and calculation errors for a representative number of samples. Using the laboratory summary form for the surrogate results, recalculate the recovery of at least one surrogate and compare the calculated value to the reported value. The two results must agree to within two significant figures.

#### **13-4. Contractual Considerations.**

*a.* Contractual considerations may impact the data review when surrogate failures are observed for laboratory control samples and blanks. A laboratory would normally be expected to reprocess a batch of field samples when a surrogate recovery is unacceptable for an LCS or blank. When surrogate recoveries for laboratory control samples or blanks are unacceptable and the batch of samples is not reprocessed, examine the Case Narrative and note why the corrective action was not performed. When surrogate recoveries for laboratory control samples and blanks grossly and systematically fail QC acceptance criteria, qualify the affected data accordingly and notify the Project Manager to determine whether to continue the PB data evaluation. (If the review were discontinued under these circumstances, the entire data package would be rejected.)

*b.* When surrogate failures are noted for environmental samples, refer to project documents such as the QAPP and the Scope of Work for analytical services to determine what corrective actions need to be documented in the laboratory's data package. Corrective actions typically performed for surrogate failures are discussed below:

(1) If matrix interference is not apparent in the chromatogram, an unacceptable surrogate recovery for an environmental sample is normally confirmed by reextracting and reanalyzing the sample. (The extract would be reanalyzed for confirmation if there were insufficient sample for reextraction.) The matrix effect is confirmed when the repeated result is within the same order of magnitude and exhibits bias in the same direction as the original result. Under these circumstances, examine the data package to determine if confirmatory analyses were performed. However, it should be noted that the laboratory may not routinely reprocess environmental samples with unacceptable surrogate recoveries unless surrogate failures in method blanks or laboratory control samples are indicative of a general method failure.

(2) When surrogate recoveries are unacceptable because of matrix interference, the laboratory may be required to perform method modifications or cleanup procedures (e.g., as described in Method 3600 of SW-846 for the SVOC analyses). Under these circumstances, examine the data package to determine if cleanups were performed. Note that when there are unacceptable surrogate recoveries followed by successful reanalyses, the laboratory is typically required to report only the successful run. When there are unacceptable surrogate recoveries followed by unsuccessful reanalyses, the laboratory is typically required to report both runs.

### 13-5. Qualification.

a. The qualification protocols for surrogate recoveries are similar to those for LCS recoveries. Qualification is generally required when the surrogate acceptance criteria of Chapter 13.2 are not met. If two surrogates are associated with (i.e., are representative of the performance of) a set of target analytes and both surrogate recoveries are unacceptable, qualify the sample result using the most noncompliant surrogate recovery. Similarly, if three or more surrogates are used and one or more surrogates are grossly out of control, then data qualification must be based upon the most noncompliant surrogate recovery. However, no action is required if three or more surrogates are used and one surrogate is marginally out of control in a sporadic manner.

b. Data qualification for noncompliant surrogate recoveries is dependent upon the direction and magnitude of the failure. Distinguish *gross* surrogate recovery failures from *marginal* failures. In the absence of more appropriate guidance, a *gross failure* is defined to occur when any surrogate recovery does not fall within 20–180% for *extractable organic* analyses and 60–140% for *purge-and-trap* analyses.

c. When a surrogate recovery for an environmental sample falls outside of the acceptance limits, the direction of bias will be said to be “well defined” when the remaining surrogates and all associated QC samples are in control or exhibit bias in the same direction. For example, if the recovery of a surrogate exceeds the upper control limit but the recoveries of other surrogates are below the lower control limit, then the direction of bias is not well defined (i.e., has not been adequately demonstrated). When there are several surrogates, a high or low recovery for a single surrogate is not necessarily indicative of the direction of bias or method extraction efficiency.

d. A direction of bias must not be inferred from the surrogate recoveries of volatiles analyzed by *purge-and-trap* (e.g., when the recoveries of all the surrogates are unacceptably low or high) unless the responses of the internal standards are available for review. Similar compounds are used for internal standards and surrogates for *purge-and-trap* analyses. The direction of bias will not be well defined when the surrogate and internal standard recoveries are not consistent with one another. For example, a high surrogate recovery can be obtained when the internal standard response (e.g., peak area) is extremely low (since the concentration of the surrogate is determined from the ratio of the surrogate response to the internal standard response).

e. In general, when the criteria of Chapter 13.2 are not met, qualify the target analytes (associated with the surrogate) as discussed below. The qualification strategies below apply (i) when two surrogates are used, (ii) and when *three or more* surrogates are used *and gross or systematic surrogate failures are observed*. These qualification strategies are illustrated in Table 13-1.

(1) “If any surrogate recovery is *marginally* unacceptable, bias *is* well defined, and there are *no gross recovery failures* for other associated surrogates, then the data must be 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. (Note that qualification is not required when three or more surrogates are used and one sporadic marginal failure is observed.)

(2) “If any surrogate recovery is *marginally* unacceptable, bias is *not* well defined, and there are *no gross recovery failures* for other associated surrogates, then the data must be qualified as follows: Qualify detections with the J flag and nondetections with the UN flag. (Note that qualification would not be required if three or more surrogates were used and one sporadic marginal failure were observed.)

(3) If any surrogate recovery is *grossly* out of control and the direction of bias is *well defined* (i.e., the recoveries of the remaining surrogates are in control or exhibit bias in the same direction), then qualify the data as follows:

(a) For *low* bias, qualify all nondetections with the R flag. If an AL is *not* specified, then qualify detections with the J- flag. If an AL is specified, then qualify detections less than the AL with the X 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 any surrogate recovery is *grossly* out of control and the direction of bias is *not* well defined, then qualify all nondetections with the R flag. If an AL is *not* specified, qualify all detections with the J flag. If an AL is specified, then 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.

**Table 13-1**  
**Data Qualification for Surrogate Recoveries <sup>1</sup>**

Sample Surrogate Recoveries	Field Sample Result (y)	Flag
%R <sub>1</sub> and %R <sub>2</sub> in control: LCL <sub>1</sub> ≤ %R <sub>1</sub> ≤ UCL <sub>1</sub> LCL <sub>2</sub> ≤ %R <sub>2</sub> ≤ UCL <sub>2</sub>	MRL < MQL < y	Flag not required
	MRL < y < MQL	J
	y < MRL	U
%R <sub>1</sub> or %R <sub>2</sub> marginally OFC with low bias: %R <sub>1</sub> < LCL <sub>1</sub> or %R <sub>2</sub> < LCL <sub>2</sub>	y > MRL	J-
	y < MRL	UN
%R <sub>1</sub> or %R <sub>2</sub> marginally OFC with high bias: %R <sub>1</sub> > UCL <sub>1</sub> or %R <sub>2</sub> > UCL <sub>2</sub>	y > MRL	J+
	y < MRL	U
%R <sub>1</sub> or %R <sub>2</sub> marginally OFC with inconsistent bias: %R <sub>1</sub> < LCL <sub>1</sub> , %R <sub>2</sub> > UCL <sub>2</sub> or %R <sub>1</sub> > UCL <sub>1</sub> , %R <sub>2</sub> < LCL <sub>2</sub>	y > MRL	J
	y < MRL	UN
%R <sub>1</sub> or %R <sub>2</sub> grossly OFC with low bias: %R <sub>1</sub> << LCL <sub>1</sub> or %R <sub>2</sub> << LCL <sub>2</sub>	y > MRL	J- X if y < AL
	y < MRL	R
%R <sub>1</sub> or %R <sub>2</sub> grossly OFC with high bias: %R <sub>1</sub> >> UCL <sub>1</sub> or %R <sub>2</sub> >> UCL <sub>2</sub>	y > MRL	J+ Possibly, X if y > AL
	y < MRL	U
%R <sub>1</sub> or %R <sub>2</sub> grossly OFC with inconsistent bias: %R <sub>1</sub> << LCL <sub>1</sub> , %R <sub>2</sub> > UCL <sub>2</sub> or %R <sub>1</sub> >> UCL <sub>1</sub> , %R <sub>2</sub> < LCL <sub>2</sub> or %R <sub>1</sub> < LCL <sub>1</sub> , %R <sub>2</sub> >> UCL <sub>2</sub> or %R <sub>1</sub> > UCL <sub>1</sub> , %R <sub>2</sub> << LCL <sub>2</sub>	y > MRL	J X if y < AL Possibly X if y > AL
	y < MRL	R

Notes: 1. It is assumed that the LOI ≤ MRL < AL. For the purposes of illustration a field sample result is evaluated using the recoveries of two surrogates. The subscripts indicate which surrogate is being referenced. For example, %R<sub>1</sub> denotes the percent recovery of the first surrogate. The following abbreviations are used: %R = Recovery of surrogate spiked into field sample; y = Concentration of a target analyte in the field sample; AL = Action Level; LCL = Lower control limit for surrogate recovery; UCL = Upper control limit for surrogate recovery; OFC = Out of control