North Carolina Wastewater/Groundwater Laboratory Certification
Matrix Spiking Policy and Technical Assistance (2/23/2018)

Policy Statement

Unless the referenced method states a greater frequency, spike 5% of samples on a monthly basis. Laboratories analyzing less than 20 samples per month must analyze at least one matrix spike (MS) each month samples are analyzed. If MS results are out of control, the results must be qualified or the laboratory must take corrective action to rectify the effect, use another method, or employ the method of standard additions. When the method of choice specifies MS performance acceptance criteria for accuracy, and the laboratory chooses to develop statistically valid, laboratory-specific limits, the laboratory-generated limits cannot be less stringent than the criteria stated in the approved method. In addition, if a MS duplicate is analyzed, the laboratory may choose to follow the method defined acceptance criteria or develop statistically valid acceptance criteria that are not less stringent than the criteria stated in the approved method.

When spiking with multi-component standards, if the method does not specify the spiking components, the following will apply.

No. of Target Analytes	Requirement
1-10	Spike All
11-20	Minimum of 10 or 80%, whichever is greater
>20	Minimum of 16

Add a concentration that is at least 10 times the MRL, less than or equal to the mid-point of the calibration curve, or method specified level to selected samples. Preferably use the same concentration as for the LFB to allow analysts to separate the matrix's effect from laboratory's performance.

The concentration of the spiked samples must be bracketed by the calibration range. If the spiked sample result is over the calibration range, the spiked sample must be diluted and re-analyzed. It is not acceptable to dilute the sample first and then add the spike solution so as not to affect bias attributed to matrix.

The volume of spike solution used in MS preparation must in all cases be ≤ 5% of the total MS volume. It is preferable that the spike solution constitutes ≤ 1% of the total MS volume so that the MS can be considered a whole volume sample with no adjustment (i.e., volume correction) by calculation necessary. If the spike solution volume constitutes >1% of the total sample volume, the sample concentration must be adjusted by calculation.

Post Digestion Spikes (PDS)

Post Digestion Spikes (PDS) are used for some analyses (e.g., metals) to assess the ability of a method to successfully recover target analytes from an actual sample matrix after the digestion process has been performed. The PDS results are used with MS results to evaluate matrix interferences. The MS and PDS should be prepared from the same environmental sample. A PDS is not to be analyzed in place of a MS. Post Digestion Spikes must be reported as post-digested and must not be misrepresented as pre-digested spikes. (Exception: TCLP and SPLP samples are always spiked post digestion.)

Parameters Excluded from MS Requirements (All Field Parameters are exempt)

- Acidity
- Alkalinity
- Bacteriological Parameters - All
- BOD/CBOD
- Chlorophyll *a*
- Color – ADMI
- Color - PtCo
- Conductivity
- Dissolved Oxygen
- Free Available Chlorine
- Hardness – Titration
- Ignitability
- Paint Filter Test
- Residues – All
- pH
- Salinity
- Sulfite
- Temperature
- Total Residual Chlorine
- Turbidity
- Vector Attraction Reduction (All Options)

Matrix Spike Technical Assistance

When spiking with multi-component standards and a subset is used, it is recommended that the spiking compounds be periodically rotated to include all compounds of interest.

Spike Preparation

The spike concentration may be set at either 5 to 50 times the Method Detection Limit (as determined by the Method Detection Limit or MDL study) for the analyte, or at 1 to 10 times the ambient level (average concentration) of the analyte in samples. There are several options for preparing spikes, for example:

> **Option 1** (Recommended - easiest) - If the spike solution volume is equal to 1% or less of the total sample volume, direct subtraction of the unspiked sample is allowed. When the volume of the standard solution spiked into a sample or a sample extract is less than 1% of the total volume then the final concentration need not be adjusted (e.g., 10 µL of spike solution added to a 1 mL final extract results in only a negligible 1% change in the final extract volume).
>
> **Option 2** - Spike volume is greater than 1% of the total spiked sample volume. In this case the sample concentration must be adjusted. When the volume of spike solution exceeds 1% of the total MS volume the sample concentration must be adjusted prior to determining spike recovery.

The general equation for Option 1 spike recovery is as follows:

$$\% R = \frac{A^* - B \times 100}{D}$$

The general equation for Option 2 spike recovery is as follows:

$$\% R = \frac{A^* - (B \times C) \times 100}{D}$$

Where:
(A) The spiked sample result
(B) Unspiked sample result
(C) % sample expressed as a decimal (sample volume used divided by final volume)
(D) Theoretical spike concentration

Note: If the spike sample is diluted, you must apply the dilution factor to the spiked sample result before calculating the percent recovery. See Option 2, Example 3.

*Note: If the sample concentration is below the reporting limit, use zero for amount of target in the unspiked sample.

To apply these general equations to the sample preparation schemes described above, refer to the following examples.

Spike Preparation Examples

Option 1 - If the spike solution volume is equal to 1% or less of the total sample volume, direct subtraction of the unspiked sample is allowed.

> **Option 1, Example 1:**
> 0.5 mL of a 1000 mg/L standard spike added to 100 mL of sample has a theoretical value of 5.0 mg/L.
>
> (A) The spiked sample result is 5.1 mg/L
> (B) If the unspiked sample result is 0.5 mg/L
> (D) Theoretical value is 5.0 mg/L

The Percent Recovery = spiked sample result (A) – unspiked sample result (B) divided by theoretical value (C) X 100; or

$$\frac{5.1 - 0.5}{5.0} \times 100 = 92\% \text{ recovery} \qquad \frac{A - B}{D} \times 100 = \text{Percent recovery}$$

Option 1, Example 2:
If the spike sample is diluted, you must apply the dilution factor to the spiked sample result before calculating the percent recovery.

1 mL of spike (concentration 250 mg/L) brought to 100 mL with sample the theoretical MS value is 2.5 mg/L. The spiked sample yielded approximately 3.1 mg/L, which is outside the upper limit of the calibration curve, so a 2X dilution was performed on the spiked sample.

(A) The diluted spiked sample result is 1.6 mg/L. After applying the 2X dilution factor, the spiked sample result is 3.2 mg/L (i.e., 2 x 1.6 mg/L = 3.2 mg/L).
(B) If the unspiked sample result is 0.5 mg/L
(D) Theoretical value is 2.5 mg/L

The Percent Recovery = spiked sample result (A) – unspiked sample result (B) divided by theoretical value (D) X 100; or

$$\frac{3.2 - 0.5}{2.5} \times 100 = 108\% \text{ recovery} \qquad \frac{A - B}{D} \times 100 = \text{Percent recovery}$$

Option 2 - Spike volume is greater than 1% of the total spiked sample volume. In this case the sample concentration must be adjusted.

Option 2 Example 1:
5 mL of spike (concentration 50 mg/L) brought to 100 mL with sample the theoretical MS value is 2.5 mg/L.

(A) The spiked sample result is 3.1 mg/L
(B) If the unspiked sample result is 0.5 mg/L
(C) % sample is 0.95 (sample volume used (95) divided by final volume (100))
(D) Theoretical value is 2.5 mg/L

The Percent Recovery = spiked sample result (A) – (unspiked sample result (B) x % sample (C)) divided by theoretical value (D) X 100; or

$$\frac{3.1 - (0.5 \times 0.95)}{2.5} \times 100 = 105\% \text{ recovery} \qquad \frac{A - (B \times C)}{D} \times 100 = \text{Percent recovery}$$

Option 2 Example 2: Larger spike volume 10 mL of spike (concentration 50 mg/L) brought to 250 mL with sample the theoretical MS value is 2.0 mg/L.

(A) The spiked sample result is 2.6
(B) If the unspiked sample result is 0.5 mg/L
(C) % sample is 0.96 (sample volume used (240) divided by final volume (250))
(D) Theoretical value is 2.0 mg/L

The Percent Recovery = spiked sample result (A) – (unspiked sample result (B) x % sample (C)) divided by theoretical value (D) X 100; or

$$\frac{2.6 - (0.5 \times 0.96)}{2.0} \times 100 = 106\% \text{ recovery} \qquad \frac{A - (B \times C)}{D} \times 100 = \text{Percent recovery}$$

Option 2, Example 3:
If the spike sample is diluted, you must apply the dilution factor to the spiked sample result before calculating the percent recovery.

5 mL of spike (concentration 50 mg/L) brought to 100 mL with sample the theoretical MS value is 2.5 mg/L. The spiked sample yielded 3.1 mg/L, which is outside the upper limit of the calibration curve, so a 2X dilution was performed on the spiked sample.

(A) The diluted spiked sample result is 1.6 mg/L. After applying the 2X dilution factor, the spiked sample result is 3.2 mg/L (i.e., 2 x 1.6 mg/L = 3.2 mg/L).
(B) If the unspiked sample result is 0.5 mg/L
(C) % sample is 0.95 (sample volume used (95) divided by final volume (100))
(D) Theoretical value is 2.5 mg/L

The Percent Recovery = spiked sample result (A) – (unspiked sample result (B) x % sample (C)) divided by theoretical value (D) X 100 or

$$\frac{3.2 - (0.5 \times 0.95)}{2.5} \times 100 = 109\% \text{ recovery} \qquad \frac{A - (B \times C)}{D} \times 100 = \text{Percent recovery}$$

Corrective Action/Qualifications for MS/MSD

Spike accuracy is usually based on a range of percent recovery (e.g., 80-120%). Spike duplicate precision is usually based on Relative Percent Difference (RPD). Refer to the method of choice for specific acceptance criteria for accuracy and precision until the laboratory develops or adopts statistically valid, laboratory-specific performance criteria. If a MS is out of established limits for either precision or accuracy, and the LCS (and other quality control) is acceptable, qualify the data for the MS sample. Repeated failures for a specific matrix may require use of an alternate method or method of standard addition. Base the sample batch acceptance on the results of the LCS analyses (and other quality control results) rather than the MS alone, because the matrix of the spiked sample may interfere with the method performance. If a MS and the associated LCS fail, re-prepare and reanalyze affected samples.

Corrective Action/Qualifications for Post Digestion Spikes

In general, if the MS recovery for an analyte does not fall within the quality control acceptance range but the PDS recovery is acceptable, then a matrix affect (associated with the preparatory process) should be suspected and the unspiked sample results must be qualified on the basis of the matrix spike recovery. However, when historical data for the effect does not exist, the laboratory would normally be expected to perform a second digestion and reanalysis of the MS to confirm the result. The result would be confirmed if the MS recoveries and PDS recoveries for both sets of analyses were similar in magnitude and bias. When both the MS recovery and PDS recovery for a particular analyte falls outside of quality control acceptance range in the same manner (i.e., the PDS and MS failures are of similar magnitude and the direction of bias is the same), confirmatory analyses are unnecessary but the data must be qualified.

Multi-component Method Spike Requirements – Quick Reference

The following provides a quick reference for the spike component requirements for multi-component methods.

- Standard Methods 6020B requires spiking all analytes of interest.
- SW-846 8000D requires spiking all analytes of interest.
- SW-846 9056A does not specify, so since there are 1-10 target analytes, all target analytes must be spiked per this policy.
- For the EPA methods, including 608.3, 624.1, 625.1, 504.1 and 1653 all target analytes of interest must be spiked. **Exception:** EPA Method 1650 requires spiking only with 2,4,6-Trichlorophenol.