Thermo SCIENTIFIC

Application Note

Tip Log #113

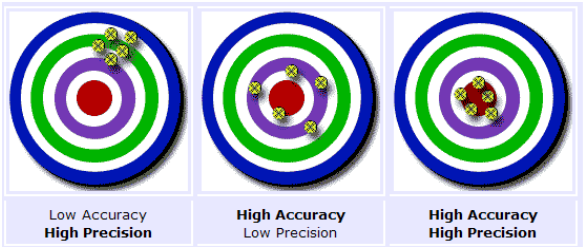
Applications Tip of the Week
Laboratory Duplicates and Matrix Spike Duplicates

We are continuing our discussion about procedures that help to ensure that the testing results are meaningful and reliable. We will focus in this Tip on Duplicate Samples and Matrix Spike Duplicates.

A Duplicate sample is a second portion (aliquot) of the same sample that is tested by using the same analytical procedures.

Why spend analytical time on repeating sample analysis?

- The analysis of the duplicate sample indicates whether we are obtaining repeatable results, or, more often we say, getting a good precision. What does precision tell us?
  - It gives us ability to evaluate quality of data.
  - Allows determining the confidence range of the results.
  - Provides a control in quality of measurements. (Signals when quality of measurements is degraded).
  - Helps to understand limitations of the data being used.
  - When comparing different methods of analysis - it allows us to choose the better analytical procedure.
- The picture below illustrates the concepts of accuracy and precision.



How to asses precision from the results of testing the sample and the duplicate

- Precision assessment is reported as Relative Percent Difference (RPD) between the two results (sample and duplicate) and calculated using the following equation:

$$\%RPD = \frac{(\text{sample result} - \text{duplicate result}) * 100}{(\text{sample result} + \text{duplicate result})/2}$$

- Here is a simple example. We got two datasets of fluoride in drinking water analysis. In the first dataset, the results for a sample and duplicate are 0.5 and 1.0 mg/L and the results for the second dataset are 1.0 and 1.1 mg/L. Looking at these data, it is intuitively clear that the second dataset of measurements is more repeatable and we have a higher level of confidence in results.
- Our next example demonstrates how the %RPD calculation helps objectively evaluate experimental precision. We use relative percent difference instead of the absolute difference in order to determine how significant the variation is. For example, in two cases, each of the following results differs by 0.8 mg/L. But for Case 1, the difference is more significant.

- Case 1: two duplicate samples read 1.2 and 2.0 mg/L.
- Case 2: two duplicate samples read 21.0 and 21.8 mg/L.

The RPD for Case 1 is 50% and the RPD for Case 2 is 3.7%. Therefore, the precision in Case 1 is poor, but the precision in Case 2 is good. Corrective action for Case 1 would be recommended. An analyst should investigate possible issues such as sample preparation, matrix interference, instrument performance, drift, sample homogeneity, accuracy of volumetric glassware, scale, rounding errors, significant figures, analyst error, contamination, etc.).

What are acceptable limits for the RPD?

Refer to the published analytical method or the laboratory standard operating procedure (SOP) for specific acceptance criteria for the acceptable RPD. For example, the EPA guidance for ATP protocol specifies the %RPD = 16% for the fluoride in wastewater analysis.

How often duplicates should be tested?

The regulatory programs specify the frequency; usually, one duplicate is recommended with each batch of 20 or fewer samples.

A Matrix spike duplicates (MSD) serve a similar purpose as sample duplicates - they allow estimating method precision for a specific sample matrix. In addition, MSD, similarly as a Matrix Spike (MS), shows the effect of the sample matrix on the accuracy of the analytical results.

How to prepare and analyze the Matrix Spike Duplicate

A matrix spike duplicate is generated the same way as a matrix spike by adding a known amount of analyte to a sample.

- In practice, three portions of a sample are prepared for testing; the first portion is for the analysis of a sample itself, the second portion is used for the matrix spike, and the third portion is used for the matrix spike duplicate analysis.
- Use steps described in the Log # 112 "Matrix Spiking – Why Spike and How to Do It" for the matrix spike duplicate preparation and analysis.

Calculation of the Matrix Spike Duplicate Results

- Matrix spike duplicate accuracy is expressed as percent recovery; it is calculated by using the same equation as for Matrix Spike:
  - $\%R = \frac{\text{(matrix spike duplicate result – unspiked sample result)} * 100}{\text{Known spike added concentration}}$

- MSD precision is expressed as relative percent difference between MS and MSD; it is calculated the same way as %RPD between a sample and sample duplicate:
  - $\%RPD = \frac{\text{(MS result – MSD result)} * 100}{\text{(MS result + MSD result)/2}}$

Interpretation of the Matrix Spike Duplicate Results

Refer to the published analytical method or the laboratory standard operating procedure (SOP) for specific acceptance criteria for MSD recovery and for %RPD. For example, the EPA guidance for ATP protocol specifies for the fluoride in wastewater analysis percent recovery between 84 and 116% and relative percent difference of 16%. If precision and accuracy is out of expected limits, investigate the possible problems and take corrective actions.