VALIDATION OF PERFORMANCE BASED ALTERNATIVES

VALIDATION PROCEDURE

QA General

- Facilities
- Personnel - training
- Equipment
- Evaluated under ISO standard or some other Laboratory accreditation program - and not dealt with in this validation protocol.
- This presentation on the inherent limitations of the method.

Assessing Bias and Precision When Reference Materials and Methods Are Not Available

- Blanks and spikes

- Spike recovery assumptions

- Comparing groups of recovery data:
  - least squares regression.

Blanks and Spikes

- If reference materials are not available – bias and variability are determined using blanks and spiked matrix blanks.

- Results compared to expected values.

- Assumptions are:
  - that the matrix blank is representative of the actual samples
  - that the spikes analyte is incorporated the same as the contaminant being measured.

Blanks and Spikes

- Accepted practices:
  - Minimum of 3 levels for the concentration range of interest.
  - At least 7 replicates at each concentration level
  - Spikes can be on positive matrices

Blanks and Spikes
Data Analysis

- One sample t procedure to the expected mean – determine a confidence interval

- Compare to an accepted recovery range – for residue analysis 80% to 120%
  - Based on professional judgment
  - Regulatory requirements

Assessing Bias and Precision When Reference Materials and Methods are Available

- Comparison to an accepted reference value
  - One sample t procedure
- Comparison to another method
  - Two sample t procedure
  - Comparing standard deviations F test

Comparison to an Accepted Reference Material

- Run the CRM 6 or more times
- Compare the mean to the CRM mean using the t statistic:

$$t = \frac{\overline{x} - \mu_0}{s \sqrt{n}}$$

  - Compare to the t statistic at the confidence level chosen (95%).

Comparison to an Accepted Reference Method

- Run 6 or more analysis of a sample using the candidate method and the reference method. Compare using the two sample t statistic.

$$t = \left(\bar{x}_1 - \bar{x}_2\right) \Big/ s\sqrt{1/n_1 + 1/n_2}$$

- Compare to the t statistic at the confidence level chosen (95%)

Comparison to an Accepted Reference Method

- Comparing two methods with several samples containing different amounts of analyte: Matched pairs t procedure

- Analyze each sample by both methods

$$t = \bar{d} \Big/ (s_d / \sqrt{n})$$

Where d_{ave} is the mean of the differences for the matched pairs and s_d is the standard deviation of these differences.

Scope and Range Requirements

- How many matrices?
  - At least one coarse and one fine soil
  - Others?
- What types of hydrocarbons
  - light –gasoline, diesel, motor oil
  - Heavy - crude oils
- What range of values?
  - 3 levels over the range of interest F1 (100 to 500) FX (500 to 1500)
  - At values required in a management scenario

Mechanics of the Process

- In house for each lab
  - Once in one lab, when one lab has verified the option, it would be accepted at other labs with demonstration of proficiency.

- At one reference lab
  - Accepted at other labs with demonstration of proficiency at other labs

- By round robin

Mechanics of the Process

- Case by case basis

- Coordinated – first in a single lab

- Front end screen

  - Procedures to take to a round robin