Spreadsheet Program for EPA's
Method 301: Field Validation of Pollutant Measurement Methods form Various Waste Media

The calculations involved in the four separate approaches in Method 301's validation protocol are incorporated into this spreadsheet. These four approaches are comparison against a validated method with paired sampling trains, method comparison with quadruplicate sampling trains, isotopic spiking with paired or quadruplicate sampling trains, and analyte spiking with quadruplicate trains. The purpose of the spreadsheet is to provide quick results to the statistical qualification tests involved with validating a method. The steps for using the spreadsheet are divided into the following sections:

A. General instructions for Lotus 1-2-3 program.
B. Method comparison with quadruplicate sampling train.
C. Method comparison with a paired sampling train.
D. Isotopic Spiking with a paired or quadruplicate train.
E. Analyte spiking with a quadruplicate sampling train.

A. General instructions for Lotus 1-2-3 program:

1. Load Lotus 1-2-3.

2. Retrieve the Method 301 program:
   * Call the menu by pressing the slash key, "/".
   * Select "FILE" (press F) then "RETRIEVE" (press R).
   * Type a: M301 (return). (Choose the drive where the PST file is located.)

3. Make selection:
   * The spreadsheet menu and title should appear: "SPREADSHEET FOR METHOD 301: VALIDATION PROTOCOL." If not press the "home" key.
   * Press "ALT" and the desired letter simultaneously.

4. Saving the spreadsheet:
   * Call up the lotus menu by pressing the slash "/."
   * Select **F**ile and **S**ave
   * Enter a filename for the saved spreadsheet, and press enter.

5. To quit Lotus:
   * press slash "/" for the menu.
   * select **Q**uit, **Y**es, and **E**xit.

B. Method comparison with quadruplicate sampling train:

1. Press "ALT" "Q" to locate this spreadsheet.

2. Enter the data for the proposed method results (both trains, A & B) and for the validated method results (both trains, A & B). To enter the data use the arrow keys to place the curser over the desired cell and key in the corresponding result. These entry cells should be unprotected and therefore blue.

NOTE: The spreadsheet was developed with the assumption that all concentration data is in comparable units, (i.e. all entries in $\mu g/m^3$ or ppm.)

3. The spreadsheet will display results for the following:

a. Proposed method variance:

$$Sp^2 = \frac{\sum_{1}^{4} (ProposedA - ProposedB)^2}{2n}$$

Proposed A: Samples from the proposed method train A.
Proposed B: Samples from the proposed method train B.
n: Number of samples.

b. Validated method variance:

$$Sv^2 = \frac{\sum_{1}^{4} (ValidatedA - ValidatedB)^2}{2n}$$

Validated A: Samples from the proposed method train A.
Validated B: Samples from the proposed method train B.
n: Number of samples.

c. Variance acceptance status:

$$IF\ Sp^2 \leq Sv^2\ THEN\ (Variance\ is\ acceptable).$$

d. Difference between Validated and Proposed results, di:

$$di = \left[\frac{(ValidatedA + ValidatedB)}{2} - \frac{(ProposedA + ProposedB)}{2} \right]$$

e. Relative standard deviation:

$$SDd = \sqrt{\frac{\sum_{1}^{4}(di-dm)^2}{n-1}}$$

dm: Average of the differences.

f. Calculated t-Value:

$$t\text{-}VALUE = \frac{dm}{\left(\frac{SDd}{\sqrt{n}}\right)}$$

g. Bias acceptance status:

IF t-VALUE(calculated) ≤ t-VALUE(critical) THEN Bias is ¬ statistically significant.

h. Correction factor:

$$CF = 1+\left(\frac{dm}{avg.\ of\ 8\ Validated\ samples}\right)$$

i. Correction factor acceptance status:

IF $(0.9 \leq CF \geq 1.1)$ *THEN CF is acceptable.*

4. Press the "home" key to return to the main menu.

C. Method comparison with a paired sampling train:

1. Press "ALT" "P" to locate this spreadsheet.

2. Enter the standard deviation of the validated method, the results for the proposed method, and the validated method results. To enter the data use the arrow keys to place the curser over the desired cell and key in the corresponding result. These entry cells should be unprotected and therefore blue.

NOTE: The spreadsheet was developed with the assumption that all concentration data is in comparable units, (i.e. all entries in $\mu g/m^3$ or ppm.)

3. The spreadsheet will display results for the following:

a. Relative standard deviation:

$$SDd = \sqrt{\frac{\sum_{1}^{9}(V-P)^2 - \frac{\left(\sum_{1}^{9}(V-P)\right)^2}{9}}{n-1}}$$

V: Validated method results
P: Proposed method results
n: Number of runs (9)

b. Standard deviation of the proposed method:

$$SDp = SDd - SDv$$

SDv: Standard deviation of validated method (given)

c. Proposed method variance:

$$Sp^2 = SDp^2$$

d. Validated method variance:

$$Sv^2 = SDv^2$$

e. Variance acceptance status:

$$IF\ Sp^2 \leq Sv^2\ THEN\ (Variance\ is\ acceptable).$$

f. Calculated t-Value:

$$t\text{-}VALUE = \frac{dm}{\left(\frac{SDd}{\sqrt{n}}\right)}$$

dm: Average difference between validated & proposed

g. Bias acceptance status:

IF t-VALUE(calculated) ≤ t-VALUE(critical) THEN

Bias is ¬ statistically significant.

Error!

h. Correction factor:

$$CF = 1+\left(\frac{dm}{avg.\ of\ 8\ Validated\ samples}\right)$$

i. Correction factor acceptance status:

IF (0.9 ≤ *CF* ≥ 1.1) *THEN CF is acceptable.*

4. Press the "home" key to return to the main menu.

D. Isotopic Spiking with a paired or quadruplicate sampling train:

1. Press "ALT" "I" to locate this spreadsheet.

2. Enter the number of samples used for the validation analysis, enter the value of the isotopic spike, and enter the results of the proposed method samples. To enter the data use the arrow keys to place the curser over the desired cell and key in the corresponding result. These entry cells should be unprotected and therefore blue.

NOTE: The spreadsheet was developed with the assumption that all concentration data is in comparable units, (i.e. all entries in $\mu g/m^3$ or ppm.)

3. The spreadsheet will display results for the following:

a. Bias:

$$B = Sm - CS$$

b. Mean:

$$Sm = \frac{\sum(Spiked\ sample\ results - CS)}{n}$$

CS: Calculated value for the isotopic spike.

c. Standard deviation:

$$SD = \sqrt{\frac{\sum(Si-Sm)^2}{n-1}}$$

Si: Individual spiked samples

d. Standard deviation of the mean:

$$SDM = \frac{SD}{\sqrt{n}}$$

n: Number of samples

e. Calculated t-Value:

$$t\text{-}VALUE = \frac{|B|}{SDM}$$

f. Bias acceptance status:

IF t-VALUE(calculated) ≤ t-VALUE(critical) THEN

Bias is ¬ statistically significant.

Critical t-VALUE ($n(12 \rightarrow 20), \alpha$ = 95%)

g. Correction Factor:

$$CF = 1 + \frac{B}{CS}$$

h. Relative standard deviation:

$$RSD = 100 \times \frac{SD}{Sm}$$

4. Press the "home" key to return to the main menu.

E. Analyte spiking with a quadruplicate sampling train:

1. Press "ALT" "A" to locate this spreadsheet.

2. Enter the value of the spiked level, enter the results of the spiked samples (both trains, A & B), and enter the results of the unspiked samples (both trains, A & B). To enter the data use the arrow keys to place the curser over the desired cell and key in the corresponding result. These entry cells should be unprotected and therefore blue.

NOTE: The spreadsheet was developed with the assumption that all concentration data is in comparable units, (i.e. all entries in $\mu g/m^3$ or ppm.)

3. The spreadsheet will display results for the following:

a. Standard deviation of the spiked samples:

$$SDs = \sqrt{\frac{\sum (SA-SB)^2}{n-1}}$$

SA: Spiked samples train A
SB: Spiked samples train B
n: Number of runs

b. Standard deviation of the unspiked samples:

$$SDu = \sqrt{\frac{\sum (SC-SD)^2}{n-1}}$$

SC: Unspiked samples train C
SD: UNspiked samples train B
n: Number of runs

c. Relative standard deviation of the spiked samples:

$$RSDs = \frac{SDs}{Sm}$$

Sm= Average of spiked samples

d. Relative standard deviation of the unspiked samples:

$$RSDu = \frac{SDu}{Sm}$$

Sm= Average of unspiked samples

e. Bias:

$$B = Sm - Mm - CS$$

f. Standard deviation of the mean:

$$SDM = \sqrt{SDs^2 + SDu^2}$$

g. Calculated t-Value:

$$t\text{-}VALUE = \frac{|B|}{SDM}$$

h. Bias acceptance status:

$$IF\ t\text{-}VALUE(calculated) \leq t\text{-}VALUE(critical)\ THEN$$
$$Bias\ is \neg\ statistically\ significant.$$

Error!

i. Correction Factor:

$$CF = 1 + \frac{B}{CS}$$

4. Press the "home" key to return to the main menu.

F. Printing options:

1. Press "ALT" "C" to locate the menu.

2. Press "ALT" "" to print the method comparison- quad train results.

3. Press "ALT" "" to print the method comparison- paired train results.

4. Press "ALT" "" to print the isotopic spiking- paired or quad train results.

5. Press "ALT" "" to print the analytye spiking- quad train results.

6. Press the "home" key to return to the main menu.