

Workbook for Standard Addition

Excel workbook *Standard_Addition_1.0.xlsm*

Author: Bo Svensmark, svensmark@plen.ku.dk, Analytical Chemistry,
PLEN, University of Copenhagen, February 2023

Short manual

The workbook works for up to 50 samples with up to 12 measurements each. The output are the unknown concentrations and statistics.

The calibration line for standard addition is always simple unweighted linear regression, because the concentration range is very limited and the extrapolation of the line below $X = 0$ must be linear.

The workbook uses macros to calculate the results in order to keep the workbook simple. A plot of the calibration function including the confidence intervals for the line can be seen, but only for one sample at a time.

Detection limit:

No detection limits (DL, LOD or LOQ) are given, since I could not find a trustworthy formula for these. Instead a concentration with a confidence interval including zero is mark as *n.d.* = not detected (the calculated concentration can still be seen in the *Xo-row* output).

Since the confidence interval is double sided, a confidence interval of 95 % corresponds roughly to a significance level of 2.5 % for detected/not detected. If you want a significance level for detection of 1 % enter 98 % in the *Confidence interval %* in cell L3.

Workflow:

- 1) To reuse the workbook, delete all values in Table 1 & 2, and the Blue and Green tables.
- 2) Do only enter data in white cells next to yellow headings
- 3) Enter *Confidence interval %* in cell L3
- 4) Enter input in Table 1 & 2
- 5) Press the button *Update*
- 6) Use the buttons *Plot data* and *Plot next* to see the graph for the sample given in *Sample #* cell H9.
- 7) Save the workbook under a new name

The workbook is protected; to unprotect go to the menu *Review* and *Unprotect* (no password needed).

Variables

Confidence interval:

The confidence interval for the determined concentrations in percent.

Table 1, input:

V_o : Volume of sample (without added standard)
 V_{total} : Total volume for constant volume, or 0 for increasing volumes (see below)
 C_s : Concentration of standard stock solution.
 V_{s1} - V_{s12} : Volume of standard added ($V_{s1} = 0$).

Table 2, input:

Y_0 - Y_{12} : Measured responses.

Blue table, output:

X_o : Sample concentration (or *n.d.* for not detected) rounded to significant digits according to sX_o . (If the last digit(s) after the decimal separator is zero, it is unfortunately not printed).
 sX_o : Standard deviation of X_o .
 $RSD\%$: relative standard deviation in percent.
 CI : Confidence interval for X_o .
 X_o -raw: Calculated concentration with 4 digits.

Green table, output:

Statistics for the calibration line. $s(y/x)$ is the residual standard deviation.

Sample #:

The index for the sample that is shown in the graph.

Grey tables:

Values for the graph. Note that X and Y in most cases are different from the input:

$$X = V_{s(input)} * C_s / V_o$$

$$Y = Y(input) * V_{total} / V_o$$

Constant volume

For standard addition with constant volume, either

1. the added volumes are so small, that they can be ignored. In this case set $V_{total} = V_o$ in Table 1
2. the volume is kept constant by addition of solvent to make up for varying volumes of standard. Enter the total volume, V_{total} in Table 1.

Increasing volumes

3. When the total volume increases enter $V_{total} = 0$ in Table 1, and the actual total volume will be calculated by $V_{total}(i) = V_o + V_{s(i)}$.

Macros:

Update: Calculate results for all samples
 Plot data: Plot the results for one of the samples (*Sample #* in cell H9).
 Plot next: Plot the results for the next sample (*Sample # +1*).

Troubleshooting

If you get an error in the macros, the Visual Basic Editor opens with an error message:

First you must reset the error:

4. Click *Ok* or *Debug* in the error message window
5. Click *Reset* (the blue square in the toolbar above the code in the VBA Editor) or *Run -> Reset*.

- Compile Error: Sub or Function not defined.
- Run-time error '1004'

This error occurs when a macro is called, and the Add-In *Analysis ToolPack - VBA* or the Add-In *Solver* is not activated.

To fix it:

6. Go to the spreadsheet and click *File -> Options -> Add-ins*
7. Now a window opens. Go to the bottom and click *Go...* next to *Manage: Excel Add-ins*
8. In the Add-ins window be sure to check the boxes next to the following Add-ins:
 - Analysis ToolPack
 - Analysis ToolPack – VBA
 - Solver Add-in

If you get an error again:

9. Click *Ok* or *Debug*
10. Click *Reset* (the blue square in the toolbar above the code)
11. Click *Tools -> Reference* and a new window opens
12. Check the boxes next to *Solver*
13. Click *Ok*, go to the spreadsheet and try to click the button causing the error again

.