ReadMe_SingleAnalyte.pdf: Outline documentation for MS Excel and Apple Notes Spreadsheets

Horwitz_Grubbs Spreadsheet - [Notes]

This is normally the last sheet - An outline with further details follows on subsequent pages.

This spreadsheet may be useful to assist Laboratory Analysts and Assessors ensure compliance with ISO/ IEC 17025:2017. The revised standard requires Measurement Uncertainty (MU) of chemical test results to be available. It is designed to help produce necessary information by using sample blanks, spikes, and comparisons with reference materials. Sample "Low Spikes" could be used to determine Recoveries and Method Detection Limits. Spikes establish MUs at different concentrations with different matrices. It may be helpful when developing new methods or for "novel" analytes and matrices. An authorised report for a single analyte can be printed.

Created with Apple "Numbers" Version 12.0, and Microsoft "Excel" 2013, spreadsheet programs - Using only "Cell Functions". No "Code", Macros, or Hyperlinks are used - **It should be "Safe" to distribute…**

The spreadsheet uses some **conventions**: In [MainTable] cells where the user is expected to input data have blue text on a white background, **bold blue** indicates that a selection is made from a list**.** Default look-ups are **grey**. Warnings are highlighted with an [**orange background**]; and critical/failure/out-of-range warnings are highlighted with [**red backgrounds**]. **Important** data is purple.

Getting Started: The sheets are [MainTable], [SampleResults], [Report], [Distributions] and [Units], and **[Notes]**. The last three are "look-ups" or information. **Data should be added or changed as outlined below…**

[**MainTable**]: Used to set the parameters of the Test:-
Fill in the Instrument/Test name that was used to create the results.
Fill in the Analyte Name for your set of results
Select Report Type from the drop-down - This will produce different a different [Report] for each type.
Select Units from the drop-down - This will change the Horwitz Ratio (larger concentrations should give higher precision).
Enter 'Spike Value' - Values between 0.00001 and 10,000,000.
MDL (From Mean of Previous Low Spikes) - If a value is entered, it will be used instead of the Results calculation.
Select Number of Significant figures - Usually **2** - 1 may be useful if near Quantitation limits, 3 for special precision.
Select One or two tail Grubbs' Test (α: 0.05) - Normally **1**; **2** is not recommended for <9 **approved** Results.
1 calculates the right and left tails separately, the furthest from the mean is used for the "one outlier" hypothesis.
Now go to the [SampleResults] Sheet…

[SampleResults]: Used to add SampleID and Results. There are 2 columns:-
Used to Add/Edit **SampleID** (or Paste from another spreadsheet).
Used to Add/Edit **Results** (or Paste from another spreadsheet).
Possible **Outliers** can be indicated by adding text e.g. Changing 77 to ?77 or 77!
This will cause the possible Outlier to be ignored by the Horwitz and Grubbs calculations.
The sheet can have many rows, but normally 3-11 are used (5, or more recommended).

[Report]: Used to display or print a formal report:-
The Report Date, Laboratory Name, Address, Contact, and Authorised data can be edited.
Check that the **Bias** and **Horwitz Ratio** are satisfactory - An Outlier can increase these values…

[Distributions]: Used to calculate Method Detection Limit (t-test) and Grubbs' critical value:-
This is not editable. It is recommended that the user consults the NIST and RSC papers, referenced in the text at the bottom of the sheet, for further background information.

[Units]: Used to calculate scale of Horwitz values, and in **[Report]** and **[Calculations - Main Table]**:-
It is normally Locked, but any changes must be reflected in **[MU Calculations]** "Select Units" drop-down.

For further information, please consult these References:-
Planning and Reporting Method Validation Studies; Supplement to EURACHEM Guide on the Fitness for Purpose of Analytical Methods, First edition 2019
Blanks in Method Validation, Supplement to EURACHEM Guide The Fitness for Purpose of Analytical Methods, First Edition 2019

The **password** to unlock individual MS Excel sheets and cells is "timstrutt" (no "quotes"). Apple Sheets use Locked "Shapes".

The **[MainTable]** uses "hidden" rows with a *red font* - Changing or deleting them will cause breakages...

Warning: Some of this content is the author's opinion. The calculations are based upon standard literature methods, but some approximations have been used. See the references described above for background information.

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SingleAnalyteMU Spreadsheet - [MainTable]

Used in conjunction with the [SampleResults] sheet. In this case the experiment is to find a reasonable MDL by using a Low Level Spike.

Results Data in [Sample Results] for Test Name	LC-MS
Analyte	Acrylamide
Report Type (Spike, Blank, Ref…)	**Low Spike**
Units	**ng/L**
Low Spike Concentration	90
MDL (From Mean of Previous Low Spikes)	
Number of Significant figures	**2**
One or two tail Grubbs' Test (α: 0.05)	**1**
Total Number of Results	9
Mean of Samples (Ymv)	80.479
ST DEV σ of Results	10.032
RSD% (CV)	12.5%
bias as %age (100 - Recovery)	10.6%
MDL Factor (n-1 Degrees Freedom)	2.896
Units - 1 Part in This Value	1.00e+12
Predicted Horwitz "Expected Value" as RSD%	22.00
Horwitz Ratio (Ideally 0.3≤ HorRat ≤1)	0.57
Ymax (Maximum Value)	89.84
Ymin (Minimum Value) may be an Outlier!	58.97
Result to 2 Significant figures	80
MDL = (MDL Factor x SD)	29
PQL (Practical Quantitation limit)	87
% Recovery	89%
Corrected for Recovery Check [Report] Sheet >>	**90 ± 32 ng/L**

For higher level experiments, this is normally filled in with the actual MDL obtained from this experiment.

HorRat looks OK…, but Grubbs' Test indicates that there may be a low outlier in SampleResults

If the suspected Outlier in SampleResults is "removed" by changing the result to "?58.97" it has a significant effect:-

Total Number of Results	9 (1 Excluded)
Mean of Samples (Ymv)	83.168
ST DEV σ of Results	6.377
RSD% (CV)	7.7%
bias as %age (100 - Recovery)	7.6%
MDL Factor (n-1 Degrees Freedom)	2.998
Units - 1 Part in This Value	1.00e+12
Predicted Horwitz "Expected Value" as RSD%	22.00
Horwitz Ratio (Ideally 0.3≤ HorRat ≤1)	0.35
Ymax (Maximum Value)	89.84
Ymin (Minimum Value)	72.11
Result to 2 Significant figures	83
MDL = (MDL Factor x SD)	19
PQL (Practical Quantitation limit)	57
% Recovery	92%
Corrected for Recovery Check [Report] Sheet >>	**90 ± 21 ng/L**

This indicates that the hypothesis that "?58.97" is an outlier is reasonable. The HorRat has improved - There appears to be no additional outliers.
The revised MDL and PLQ values can probably be used, but consider 7 Spikes at an even lower level, say, at 50ng/L, and at least 7 "Blanks" (US EPA821-R-16_006).

SingleAnalyteMU Spreadsheet - [SampleResults] Used with the [MainTable] sheet.

S1	86.38
S2	87.79
S3	77.94
S4	72.11
S5 Duplicate S3	78.56
S6	89.84
S7	89.30
S8	83.42
S9 (Outlier?)	58.97

HorRat looks OK…, but Grubbs' Test indicates that this may be a low outlier - Adding alpha characters will exclude it : ?58.97

Data can be manually entered into this sheet, or copied/pasted from another spreadsheet (paste raw results only not formulae). It is also possible to link to a CSV/MS_Excel file or database, but remember to use the starting address as the sheet's top 1,1 corner (R1,C1?). Any result with an alpha character (a-z,!@#$%^&*, etc.,) will not be included in calculations. Copy cells from other spreadsheets as plain text, otherwise formatting could be lost...

SingleAnalyteMU Spreadsheet - [Report]

Used in conjunction with the [SampleResults] sheet.
This can be filed as a PDF, or a copy sent out…

Summary Report - Low Spike	
Report Date	25 April 2022
Laboratory Name	Tim's Testing & Consulting Laboratory Pty Ltd
Address	15a Bridge Street Some-Town, STATE, X100
These cells can be edited… Contact	Tim Strutt e.g. tcstrutt+horwitzt@gmail.com
Authorised By	Saga Brondam
Analyte	Acrylamide
Number of Samples in This Report	8
Report Type	Low Spike
	Editable text for Reference Materials can be added here - e.g. Certified value, catalogue and batch number, expiry date …
Low Spike Level	90 ng/L
% Recovery	92%
RSD% (CV)	0.1
Bias as a %age	0.1
Is Bias Satisfactory? Y/N	Yes ← *Must be approved for final formal report…*
Horwitz Ratio (Ideally 0.3≤ HorRat ≤1)	0.35
Is Horwitz Ratio Satisfactory? (Y/N):	Yes ← *Must be approved for final formal report…*
Result to 2 Significant figures	83 ng/L
Method Detection Limit (MDL)	19 ng/L
Practical Quantitation Limit (PQL)	57 ng/L
Result Corrected for Recovery Bias	**90 ± 21 ng/L**

SingleAnalyteMU Spreadsheet - [Distributions]

This is the fourth Sheet

This is used to by **[Main]** to look up Horwitz Ratio and Grubbs' test values. It cannot be edited.

SingleAnalyteMU Spreadsheet - [Units]

This is the fifth Sheet

This is used to by **[Main]** to look up Units concentration values. - It can be edited.

It contains many common units. Values cover a range from ~ 10% to Parts-per-Trillion (ppt).

If required additional units may be added; but, as noted "Units" in the **[Main]** sheet must be updated.
