Expressing uncertainty as Uncertainty Factor, and Combining sampling and analytical uncertainty

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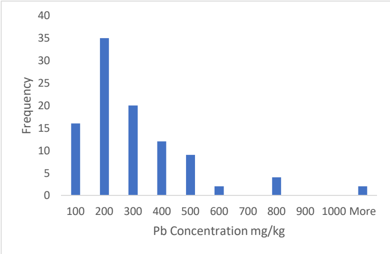

Eurachem/Eurolab Workshop,
Uncertainty from sampling and analysis for accredited laboratories
November 2019, Berlin

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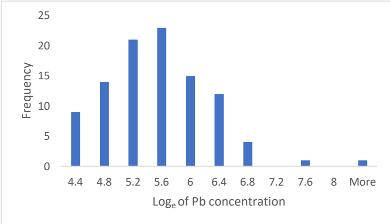

Overview

- What is the Uncertainty Factor (^{F}U) ?
- How to calculate the Uncertainty Factor
- Worked example applying the Uncertainty Factor
- Advantages of using the Uncertainty Factor
- How to combine UfS as Uncertainty Factor, with analytical uncertainty (UfA)
- Conclusions

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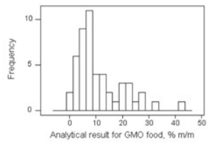
What is the Uncertainty Factor (^{F}U) ?

- ^{F}U is alternative way to express measurement uncertainty, more accurate when :-
  - Relative expanded uncertainty value is large (e.g. > 20%) where
  - Frequency distribution of the uncertainty is approximately log-normal rather than normal.
- These two conditions often apply to measurement uncertainty that arises from sampling process,
  - particularly when spatial distribution of analyte in test material is substantially heterogeneous.
- Can also apply to purely analytical systems, e.g.
  - GMO (genetically modified organism) in soya by PCR (polymerase chain reaction
  - distribution lognormal, RSD = 0.7 (i.e. 70%) from PT (AMC_TB#18*)



- Upper and lower confidence limits of a measurement value, are expressed by:
  - multiplying and dividing the measurement value by ^{F}U, rather than by
  - adding and subtracting the uncertainty (U).

*AMC (2004) Technical Brief Number 18. GMO Proficiency testing: Interpreting z-scores derived from log-transformed data

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How to calculate the Uncertainty Factor

- Standard uncertainty factor (^{F}u) calculated* as

$$^{F}u = \exp(s_G) = e^{s_G}$$

  - where s_G is the standard deviation of the $\log_e$-transformed measurement values (x)

$$s_G = s(\ln(x)) = s(\log_e(x))$$

- Expanded uncertainty factor (^{F}U), for 95% confidence, calculated as

$$^{F}U = \exp(2s_G) = e^{2s_G}$$

- Updated worked Example A2, for Pb-contaminated soil
  - shows how ^{F}U evaluated in practice using 'duplicate' method.

*Ramsey M.H. Ellison S.L.R (2015) Uncertainty Factor: an alternative way to express measurement uncertainty in chemical measurement. Accreditation and Quality Assurance: Journal for Quality, Comparability and Reliability in Chemical Measurement. 20, 2,153-155. doi:10.1007/s00769-015-1115-6

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Example A2: Estimation of UfS in soil - using Duplicate Method

Scenario:
- Former landfill, in West London
- 9 hectare = 90 000 m^2
- Potential housing development
- measurand → [Pb] in each sampling target

Area of investigation:
- 300 m x 300 m area → depth of 0.15 m
- 100 sampling targets in a regular grid (10 x 10)
- 100 primary samples (taken with soil auger)
  - each intended to represent a 30 m x 30 m target

Application of Duplicate Method to estimate UfS

Figure 1: A balanced design

Sampling target

Sample 1 | Sample 2

Analysis 1 | Analysis 2 | Analysis 1 | *Analysis 2*

10% of targets in whole survey

→ between-target variance

between-sample variance

between-analysis variance

- Duplicate samples taken at 10/100 sampling targets (i.e. 10%)
  - randomly selected.
  - Duplicate sampling point 3 m from the original sampling point
    - within the sampling location,
    - in a random direction
    - within the sampling target

Application of Duplicate method to estimate UfS

- Aims of design of duplicate taking to reflect:-
  - ambiguity in the sampling protocol
    - how differently could it be interpreted by a different samplers?
  - uncertainty in locating sampling location within sampling target
    - e.g. survey error by using tape and compass
  - effect of small-scale heterogeneity within each sampling target on measured concentration
    - e.g. at 10% of grid spacing distance, 3m for 30m

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Sample prep and analysis in the lab

- Soil samples dried, sieved (<2 mm), ground (<100 μm)
- Test portions of 0.25g digested in nitric/perchloric acid
- [Pb] measured with ICP-AES, under full AQC
- 6 soil CRMs measured to estimate analytical bias over range of concentration
- corrected for reagent blank concentrations where statistically different to zero
- Raw measurements for use for estimation of uncertainty were:
  - **untruncated** – e.g. 0.0124 mg/kg, not < 0.1 or < detection limit
  - **unrounded** – e.g. 2.64862 mg/kg, not 3 mg/kg

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Spatial Map of Measured Pb concentration

Row	A	B	C	D	E	F	G	H	I	J
1	474	287	250	338	212	458	713	125	77	168
2	378	3590	260	152	197	711	165	69	206	126
3	327	197	240	159	327	264	105	137	131	102
4	787	207	197	87	254	1840	78	102	71	107
5	395	165	188	344	314	302	284	89	87	83
6	453	371	155	462	258	245	237	173	152	83
7	72	470	194	83	162	441	199	326	290	164
8	71	101	108	521	218	327	540	132	258	246
9	72	188	104	463	482	228	135	285	181	146
10	89	366	495	779	60	206	56	135	137	149

Argyraki (1997)

- Measured Pb concentration ranges from 56 to 3590 mg kg^{-1}
- Straddles then UK threshold of 450 mg Pb kg^{-1} for action required (further risk assessment)
- Uncertainty of measurements estimated by taking of Duplicate Samples at 10% of sampling targets

Measurements from balanced design for UfS estimation

Sampling target

Sample 1 | Sample 2

Analysis 1 | Analysis 2 | Analysis 1 | *Analysis 2*

- Large differences between some sample duplicates (e.g. D9) = high level of UfS
- Good agreement between analytical duplicates (< 10 % difference)

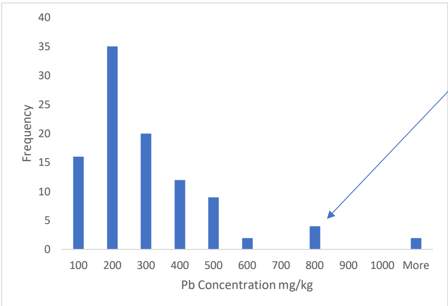
Target #	S1A1	S1A2	S2A1	S2A2
A4	787	769	811	780
B7	338	327	651	563
C1	289	297	211	204
D9	662	702	238	246
E8	229	215	208	218
F7	346	374	525	520
G7	324	321	77	73
H5	56	61	116	120
I9	189	189	176	168
J5	61	61	91	119

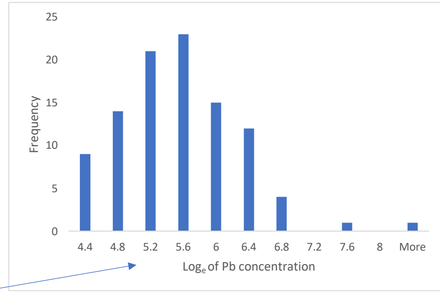
mg kg^{-1}

- Needs inspection of frequency distribution to select the best approach to UfS estimation

Estimating the Uncertainty as ^{F}U - Histograms

- Frequency distribution of [Pb] across the site = long range heterogeneity
- Distribution of Pb measurements on 100 sampling targets is positively skewed = approximately log-normal
- Log-transformation necessary to remove skew





- Distribution closer to Normal after $\log_e$ transformation

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Estimating the Uncertainty as ^{F}U - Scatter Plots

Frequency distribution of [Pb] between sample duplicates

mainly due to within-target (short range) heterogeneity.

Pb concentration values made on duplicated samples (10 of 100 targets) in either:-

(a) original concentration units

Duplicate samples (S1 , S2) generally differ by more than the duplicate analyses (A1 and A2 in same colour) - as seen in Table

(a) Four targets (2, 4, 6 and 7) have particularly large difference between duplicate samples, suggesting a positively skewed distribution for sampling uncertainty,

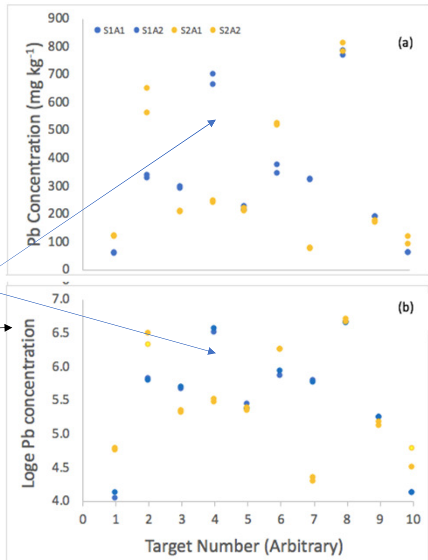
- like that between the targets (Histogram #1).

e.g. D9

(b) $\log_e$ transformed

Values show generally much smaller differences, more similar across range of concentration.

Distribution made closer to normal by log transformation (like Histogram #2).



Analytical Methods Committee (2019). Why do we need the uncertainty factor? Technical Brief 88, 27. DOI: http://dx.doi.org/10.1039/c9ay90050k Anal. Methods, 2019, 11, 2105–2107
https://pubs.rsc.org/en/content/articlelanding/2019/ay/c9ay90050k#!divAbstract

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Need for log-transformation?

- Classical analysis of variance (ANOVA) assumes approximately normal distributions
- Robust ANOVA can accommodate up to 10% outlying values,
  - but not more, and not heavy skew
- Use of log-transformation (where there is a log-normal distribution), can:
  1. Avoid issue, when uncertainty is large (e.g. *u'* over 50 %), that lower confidence limit are negative = clearly impossible (i.e. when a normal distribution is assumed erroneously)
  2. Compensates for any approximate proportional change of U with increasing concentration
  3. Enables justified use of Classical ANOVA (if log-transform produces a near normal distribution)
- However, once transformed, measurement values (and ANOVA results) are no longer given in input units of concentration (e.g. mass fraction, mg kg $^{-1}$)

Measurement values of Pb concentration

In mg kg^{-1}

Target #	S1A1	S1A2	S2A1	S2A2
A4	787	769	811	780
B7	338	327	651	563
C1	289	297	211	204
D9	662	702	238	246
E8	229	215	208	218
F7	346	374	525	520
G7	324	321	77	73
H5	56	61	116	120
I9	189	189	176	168
J5	61	61	91	119

log$_e$-transformed

Target #	S1A1	S1A2	S2A1	S2A2
A4	6.67	6.65	6.70	6.66
B7	5.82	5.79	6.48	6.33
C1	5.67	5.69	5.35	5.32
D9	6.50	6.55	5.47	5.51
E8	5.43	5.37	5.34	5.38
F7	5.85	5.92	6.26	6.25
G7	5.78	5.77	4.34	4.29
H5	4.03	4.11	4.75	4.79
I9	5.24	5.24	5.17	5.12
J5	4.11	4.11	4.51	4.78

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RANOVA2 output for Soil Example A2

Classical ANOVA

Mean	*317.8*		No. Targets	*10*
Total Sdev	*240.19*			
	Btn Target	Sampling	Analysis	Measure
Standard deviation	*197.55*	*135.43*	*17.99*	*136.62*
% of total variance	*67.65*	*31.79*	*0.56*	*32.35*
Expanded relative uncertainty (95%)		*85.23*	*11.32*	*85.98*
Uncertainty Factor (95%)		*2.6032*	*1.12*	*2.6207*

Robust ANOVA

Mean	*297.31*			
Total Sdev	*218.49*			
	Btn Target	Sampling	Analysis	Measure
Standard deviation	*179.67*	*123.81*	*11.144*	*124.31*
% of total variance	*67.63*	*32.11*	*0.26*	*32.37*
Expanded relative uncertainty (95%)		*83.29*	*7.50*	*83.63*

- Software RANOVA2* (in Excel) performs Classical and Robust ANOVA
- Classical ANOVA output gives poor estimate of *U'* = 85.98%,
- but also estimate of ^{F}U as 2.62 (after log$_e$-transformation)
- Transformation can be either to base 'e' or to base 10,
  - log$_e$ has some advantages (discussed below), and is recommended.

Robust U as 83.63% (for comparison)
Inspection of histogram suggests > 10% of outlying values, so direct classical, and robust estimate are not very reliable
So log-transformation before classical ANOVA is likely to be a better option

- **There are 2 options for implementation: -**

1. Use this RANOVA2, which does log$_e$ transformation internally and calculates ^{F}U directly
2. Make log$_e$ transformation externally (e.g. in Excel) and then use Classical ANOVA
   - but most other ANOVA packages don't calculate the required component variances directly

* http://www.rsc.org/Membership/Networking/InterestGroups/Analytical/AMC/Software/

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Calculation of the Uncertainty Factors - Internal

Classical ANOVA

Mean	*317.8*		No. Targets	*10*	
Total Sdev	*240.19*				
	Btn Target	Sampling	Analysis	Measure	
Standard deviation	*197.55*	*135.43*	*17.99*	*136.62*	
% of total variance	*67.65*	*31.79*	*0.56*	*32.35*	
Expanded relative uncertainty (95%)		*85.23*	*11.32*	*85.98*	
Uncertainty Factor (95%)		*2.6032*	*1.12*	*2.6207*	

- Classical ANOVA on raw data using 'RANOVA2' gives:
- ${}^{F}U_{sampling}$ = 2.60 = expanded uncertainty factor of the sampling
- ${}^{F}U_{analysis}$ = 1.12 = expanded uncertainty factor of the analysis – *really analytical repeatability*
- ${}^{F}U_{meas}$ = 2.62 = expanded uncertainty factor of the measurement
- Sampling accounts for 98% (31.79/32.35) of the measurement uncertainty

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External calculation of ${}^{F}U$

Classical ANOVA output when applied to natural logarithms of the measured concentration values

Target #	S1A1	S1A2	S2A1	S2A2
A4	6.67	6.65	6.70	6.66
B7	5.82	5.79	6.48	6.33
C1	5.67	5.69	5.35	5.32
D9	6.50	6.55	5.47	5.51
E8	5.43	5.37	5.34	5.38
F7	5.85	5.92	6.26	6.25
G7	5.78	5.77	4.34	4.29
H5	4.03	4.11	4.75	4.79
I9	5.24	5.24	5.17	5.12
J5	4.11	4.11	4.51	4.78

Mean	*5.478*			
Total Sdev	*0.82337*			
	Btn Target	Sampling	Analysis	Measure
Standard deviation	*0.66775*	*0.4784*	*0.0567*	*0.4817*
% of total variance	*65.77*	*33.76*	*0.47*	*34.23*

Mean value in log-space (5.478), gives geometric mean of 239.4 mg/kg = $e^{5.478}$

Measurement standard deviation of $\log_e$-transformed values, $s_{G,meas}$ = 0.4817

Standard uncertainty factor ${}^{F}u = \exp(s_G) = e^{0.4817} = 1.6189 = 1.62$

Expanded uncertainty factor ${}^{F}U = \exp(2s_G) = e^{2*0.4817} = 2.6207$ **= 2.62** ${}^{F}U = ({}^{F}u)^2 = (1.62)^2$

- Value of ${}^{F}U$ same as that calculated internally and automatically by RANOVA2

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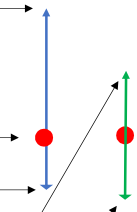
Confidence Limits on Measurement Value

- *For* $^{F}U = 2.62$, for a typical Pb measurement value of 300 mg kg^{-1}

Upper confidence limit (UCL) = 784 mg kg^{-1} (300 x 2.62)



Measurement value of 300 mg kg^{-1}

- Lower confidence limit (LCL) = 115 mg kg^{-1} (300 / 2.62)
- Asymmetric confidence limits around the measured value
- -185 and +484 mg kg^{-1} (away from 300)
- Reflects skew in frequency distribution of the uncertainty as seen in scatter plot & histograms -

- Not seen in symmetrical confidence limits from robust U' = 83.6% = 251 (300 * 0.836)
- = +/- 251 mg kg^{-1} UCL = 551 (300 + 251)
- LCL = 49 (300 - 251)
  - calculated without log-transformation.

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Combining $^{F}U_{sampling}$ with analytical uncertainty as $U'_{analysis}$

Two options* for combining uncertainty factor ($^{F}U_{samp}$) with relative uncertainty ($U'_{analysis}$)

- For example when ($U'_{analysis}$) is from a different estimation process:-

Option 1: Have both sampling and analytical uncertainty components calculated and expressed in log-domain. MOU15

- happens automatically when ANOVA is performed on log-transformed measurement values.

Option 2: For analytical component, use approximation (#1, from GUM**) that relative standard uncertainty ($s'_{analytical}$) is equal to standard deviation of natural logarithms ($s_{G,analytical}$)

- $s'_{anal} \approx s_{G,anal}$ $s_{G,anal} \approx s'_{anal}$
- Approximation acceptable when $s'_{analytical} < 0.2$, - usually the case.
- Two components can then be added as variances in log-space, as in Option 1.
  - Worked case study based on Example A2

*Ramsey M.H. and Ellison S.L.R (2017) Combined uncertainty factor for sampling and analysis. Accreditation and Quality Assurance: Journal for Quality, Comparability and Reliability in Chemical Measurement, 22(4), 187-189). DOI 10.1007/s00769-017-1271-y
http://www.springer.com/-/0/AVxRKJMqXBkgGLWLEZQa

**GUM (2007) JCGM 101, Evaluation of measurement data — Supplement 1 to the "Guide to the expression of uncertainty in measurement" — Propagation of distributions using a Monte Carlo method

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Slide 18

MOU15 Say from external source
Microsoft Office User, 14/10/2019

Combining $^{F}U_{sampling}$ with analytical uncertainty as $U'_{analysis}$

Summation of uncertainties:-

- for standard measurement uncertainty $u_{meas} = s_{meas} = \sqrt{s_{anal}^2 + s_{samp}^2}$
- Similarly, for relative standard measurement uncertainty $s'_{meas} = \sqrt{(s'_{anal})^2 + (s'_{samp})^2}$
- So in log–space, analogous calculation (using sG values) is:- $s_{G,meas} = \sqrt{s_{G,samp}^2 + s_{G,anal}^2}$
  used in ANOVA of log-trans values for Option 1

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Combining $^{F}U_{sampling}$ with analytical uncertainty as $U'_{analysis}$

- As $^{F}u = \exp(s_G)$ where $s_G = s(\ln(x))$ = standard deviation of the $\log_e$-transformed measurement values
- Standard uncertainty factor $^{F}u_{meas} = exp(s_{G,meas}) = exp\sqrt{s_{G,samp}^2 + s_{G,anal}^2}$
  - $^{F}u_{meas} = \exp\sqrt{(\ln(^{F}u_{samp}))^2 + (\ln(^{F}u_{anal}))^2}$ harder to add as standard uncertainty factors
- $s_{G,anal} \approx s'_{anal}$ when $s'_{anal} < 0.2$ (Approximation #1)
- So use s'_{anal} as an approximation for $s_{G,anal}$ in $^{F}u_{meas}$ equation, which becomes:-
- $s_{G,meas} \approx \sqrt{s_{G,samp}^2 + (s'_{anal})^2}$
- $\boldsymbol{^{F}u_{meas} = exp\sqrt{s_{G,samp}^2 + (s'_{anal})^2}}$ - useful equation for addition using **Option 2**

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Combining $^{F}U_{sampling}$ with analytical uncertainty as U'$_{analysis}$

For Example A2

$s_{G,samp} = 0.4784$
and $s_{G,anal} = 0.0567$

Mean	5.478				
Total Sdev	0.82337				
	Btn Target		Sampling	Analysis	Measure
Standard deviation	0.66775		0.4784	0.0567	0.4817
% of total variance	65.77		33.76	0.47	34.23

Classical ANOVA of log-transformed values

Option 1.

$s_{\text{G,meas}} = 0.4817$ ………using $s_{\text{G,meas}} = \sqrt{s^2_{\text{G,samp}} + s^2_{\text{G,anal}}}$

$^{F}u_{\text{meas}} = \mathbf{1.6189}$ ………using $^{F}u_{\text{meas}} = \exp\sqrt{s^2_{\text{G,samp}} + s^2_{\text{G,anal}}}$

Option 2. Considering the analytical uncertainty as normally distributed,

s'_{anal} value = 0.0566 (e.g. from classical ANOVA of raw values, U'$_{anal}$ =11.32% , /200), which gives

$^{F}u_{\text{meas}} = \mathbf{1.6188}$ ……using $^{F}u_{\text{meas}} = \exp\sqrt{s^2_{\text{G,samp}} + (s'_{\text{anal}})^2} = \exp\sqrt{0.4784^2 + 0.0566^2}$

Estimates of ^{F}u virtually identical by both options (1.6189 ~ 1.6188) so
Expanded $^{F}U = (^{F}u)^2 = 2.62$

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Inclusion of analytical bias in $^{F}U_{meas}$ estimate

- Analytical bias - modelled as Linear functional relationship fitted between measured values on certified values of 6 CRMs (using FREML*)

  \- 3.41 % ± 1.34 %

- Systematic component of relative expanded uncertainty:

  $u_{systematic}{}' = \sqrt{-3.41^2 + 1.34^2}$ % = 3.72 %

  $s'_{\text{systematic}} = 0.0372$ mg kg^{-1}

- Currently no consensus on how to combine systematic and random components of uncertainty.
- One method is to add them by the sum of their squares (extending previous equation):
- $^{F}u_{\text{meas}} = exp\sqrt{s^2_{\text{G,samp}} + (s'_{\text{anal}})^2 + (s'_{systematic})^2}$
- $\exp\sqrt{0.4784^2 + 0.0566^2 + 0.0372^2}$ = 1.621 (up from 1.619)
- $^{F}U = (^{F}u)^2 = 2.628$ (up from 2.621)

*Functional Relationship Estimation by Maximum Likelihood, AMC Technical Brief Number 10 (2002), software from:- https://www.rsc.org/Membership/Networking/InterestGroups/Analytical/AMC/Software/

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Relative U & Uncertainty Factor – *Approximation #2*

MOU16

- Relative uncertainty u', expressed as a fraction, can be calculated from Approximation #2*

$$u' = \sqrt{\exp(s_G^2) - 1}$$

- *For for Example A2,* $s_{G,anal} = 0.05668$

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- Using approximation formula, $u'_{\text{anal}} = 0.05673$ (s'_{anal} value = 0.05661, from classical ANOVA)
- Approximation inaccurate if $s_G > 0.5$

* know feature of log-normal distribution, e.g.

Johnson, N. L., Kotz, S. and Balakrishnan, N. (1995) _Continuous Univariate Distributions_, volume 1, chapter 14. Wiley, New York.

https://en.wikipedia.org/wiki/Log-normal_distribution

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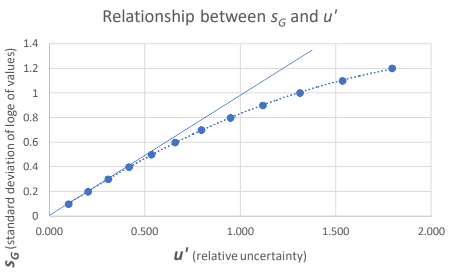
Relative U & Uncertainty Factor – *Approximation #2*



s_G	u'
0	0.000
0.1	0.100
0.2	0.202
0.3	0.307
0.4	0.417
0.5	0.533

$$u' = \sqrt{\exp(s_G^2) - 1}$$

Useful agreement between s_G and u' up to around $s_G = 0.4$ ($u' = 0.42$)
- *Marginal for Example A2 for* $s_{G,\text{meas}} = 0.4817$

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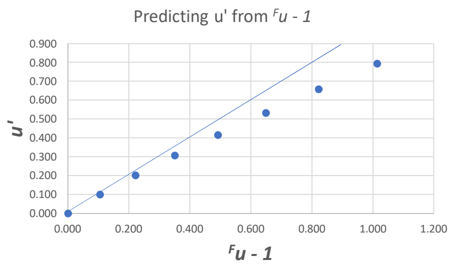
Slide 23

MOU16 Source of this equation?
Microsoft Office User, 14/10/2019

MOU17 Make sources of all values clearer
Microsoft Office User, 14/10/2019

Relative U & Uncertainty Factor *– Approximation #3*



Even rougher approximation, by observation, that:

$$u' \approx {}^Fu - 1$$

- u'_{anal} in Example = 0.0566 ≈ (1.0583 – 1) = 0.0583
- i.e. 3% overestimate here, 10% at 0.2 - but useful rough guide
- Gives intuitive appreciation of ^Fu and ^FU values
  - e.g. ^FU = 1.05 is roughly equivalent to U' = 5% - really ~4.9%
  - ^FU = 1.10 " U' = 10% - really ~9.5%
  - ^FU = 1.15 " U' = 15% - really ~14%

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Conclusions

- Uncertainty Factor (^FU) is a useful alternative way to express measurement uncertainty
- Particularly useful for expressing UfS, when
  - Uncertainty values are high (>20%)
    - e.g. due to substantial heterogeneity of analyte concentration (within or between-target)
  - When frequency distribution is visibly log-normal (e.g. highly skewed)
- ^FU can also apply to purely analytical sources, when U' is high (>20%)
  - e.g. GMO in soya by PCR
- Also allows for possible variation of U, with U proportional to concentration
- Never gives a negative Lower Confidence Limit
- Gives more accurate Confidence Limits for make assessments of compliance
- ^FU is harder to explain, but maybe approximations can make it more accessible

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