

contaminated 30 ha site.² The histogram of the frequency distribution of the measurement values shows a positively skewed distribution (Fig. 1a), but when natural logarithms of the measurements are taken, the distribution becomes approximately normal (Fig. 1b).

The uncertainty of each of these measurements was estimated using the 'duplicate method', in which duplicated analytical measurements are taken on duplicated samples taken at 10 of these 100 targets¹ (Fig. 2).

The estimate of the expanded relative measurement uncertainty, made using analysis of variance (ANOVA) on the original measurements,² was 83.9%. However, inspection of the differences between the 10 duplicate samples (Fig. 2a) reveals evidence of the same positive skew seen for the 100 targets (Fig. 1a), with a substantial proportion of large differences (4/10 by a factor of ≥ 1.5). The implication is that the nature of the heterogeneity between the targets is similar to that between the sample duplicates within a target, which affects the frequency distribution of the uncertainty from sampling. To overcome this problem, the ANOVA was applied to the natural logarithms of the 40 measurements made on the 10 duplicated samples (Fig. 2b).

The initial estimate of uncertainty of the log-transformed measurement (s_L) is

still 'in log space'; that is, expressed on the same logarithmic scale as the log-transformed data. To make the resultant estimate of the measurement uncertainty useful in the linear domain, it can be expressed as a (standard) *uncertainty factor* ($^F u$), for the 68% confidence interval.³

$$= s_L \cdot () \quad (1)$$

For the more usual 95% confidence, this is expressed as an *expanded uncertainty factor* ($^F U$). The value of $^F U$ can be calculated, either by multiplying s_L by the coverage factor of two ($k = 2$) in the log-domain or, equivalently, by raising $^F u$ to the power of k .

$$= s_L \cdot (\times) = () \quad (2)$$

To use the uncertainty factor, the lower 95% confidence limit is calculated

by *dividing* the measurement value by $^F U$, and the upper limit by *multiplying* the measurement value by $^F U$.

For this example, the value of s_L is 0.48, $^F u$ is calculated as 1.62 using eqn (1), and $^F U$ is 2.62 using eqn (2).⁴ For a typical measured lead concentration value of 300 mg kg^{-1} , the lower 95% confidence limit is 115 mg kg^{-1} (*i.e.*, $300/2.62$) and the upper confidence limit is 784 mg kg^{-1} (*i.e.*, 300×2.62).

This confidence interval is from 115 to 784 mg kg^{-1} , which is from -185 to $+484 \text{ mg kg}^{-1}$ away from the measurement value. This interval is clearly asymmetric and reflects the positive skew seen in the original measurements (Fig. 1a).

A further advantage of the uncertainty factor, is that it always gives positive values for the confidence limits of an uncertainty estimate. This contrasts with naïve approaches to high relative uncertainty, which can easily imply an expanded uncertainty extending well below zero.

An apparent complication can arise when the measurement uncertainty from the chemical analysis is expressed as relative uncertainty, but that from the sampling is expressed as an uncertainty factor. However, two solutions to this issue of combining uncertainty expressed in two different ways have been identified.⁴ One option is to also express the uncertainty from chemical analysis as an uncertainty factor, to match that from the sampling. This option enables a valid combination of the two uncertainties to be made in the usual way, but in log space, producing a combined uncertainty factor for the whole measurement process.

the measurement value by the factor. This contrasts with the approach of adding and subtracting the uncertainty value from the measurement value, for the Gaussian (normal) situation. The uncertainty factor is particularly applicable to higher levels of uncertainty, and it also allows for the increase of standard uncertainty as a function of concentration.

Organization for Standardization, Geneva.

2 *Eurachem/EUROLAB/CITAC/Nordtest/ AMC Guide: Measurement uncertainty arising from sampling: a guide to methods and approaches Eurachem*, ed. M. H. Ramsey and S. L. R. Ellison, 2007, p. 40, ISBN 978 0 948926 26 6, Example A2.

3 M. H. Ramsey and S. L. R. Ellison, Uncertainty Factor: an alternative way to express measurement uncertainty in chemical measurement, *Accredit. Qual. Assur.*, 2015, 20(2), 153–155, DOI: 10.1007/s00769-015-1115-6.

4 M. H. Ramsey and S. L. R. Ellison, Combined uncertainty factor for sampling and analysis, *Accredit. Qual. Assur.*, 2017, 22(4), 187–189, DOI: 10.1007/s00769-017-1271-y.

Michael H. Ramsey

A B C
A C E
13 2019.

Further reading

1 ISO 3534-1 (1993a), Statistics – vocabulary and symbols, International



Published on 27 March 2019. Downloaded on 4/15/2019 5:33:31 PM.