Consulting Analytical Chemists and Geochemists

THE PURPOSE OF UNCERTAINTIES IN THE COMPARISON OF ANALYTICAL RESULTS

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1 Principles of Uncertainty

The principles of uncertainty in measurement comprises of several considerations. Since all measurements have uncertainties, two analyses of the same quantity will rarely give the same value. Knowledge of the uncertainty of the measurements allow comparison between different quantities, by seeing if they agree within their uncertainties. Once analytical values agree within their uncertainties, it can be inferred that the difference is entirely explained by their measurement uncertainties. Conversely, when values do not agree within their uncertainties it means that the difference observed cannot be explained by the measurement uncertainties alone. In this latter scenario, the differences are likely to be due to some constant bias in the method, or as a result of gross error, e.g., sample swap.

1.2 Using Measurement Uncertainty

1.2.1 Example 1: Comparing Two Means

Two measurements of the same quantity will rarely give the same value. For example, two analysts perform an analysis of lead in triplicate in the same soil sample. The mean values obtained their respective uncertainties as 1-sigma and 2-sigma standard deviations are given below. Are the means statistically different?

$$Alice: 10.1 \pm 0.3\, ppm$$
$$Bob: 9.6 \pm 0.4\, ppm$$

$$10.1 - 0.3 = 9.8\ (Minimum)$$
$$9.6 + 0.4 = 10\ (Maximum$$

Since the means *both include* the *range* of values from 9.8 to 10 ppm, we can say that the means agree *within their* experimental uncertainties. Therefore, whenever two quantities with uncertainties have a range, or even a single value in common, we say that they are within their experimental uncertainties.

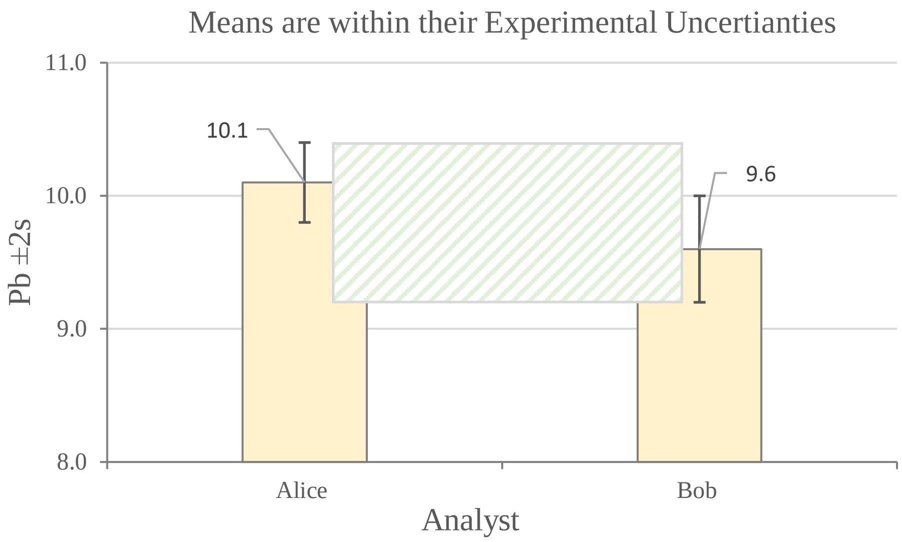

Figure 1. Mean Pb±2 standard deviations for two different analysts. Since the two Pb values and their uncertainties have a range (green pattern fill) in common, they are within their experimental uncertainties and are therefore equal.

1.2.2 Example 2: Comparing a Mean and a Certified Value

A similar approach can be used to compare the mean value of a series of replicate analyses of a certified reference material and the given certified value.

A new procedure for the rapid analysis of sulphur in kerosene was tested by the analysis of a certified reference material of kerosene with a given certified value (as per the certificate of analysis) of 0.123% S. The results obtained were: %S=0.112, 0.118, 0.115, and 0.119, with a standard deviation of 0.0033.

Do the data indicate the presence of a negative systematic error in the new method?

The statistical treatment for this type of problem involves comparing the difference $(\bar{x} - \mu)$ with the difference that would normally be expected as a result of the random uncertainty (equation [1]). If the observed difference, *i.e.*, $(\bar{x} - \mu)$ is *less than* that which is calculated at say, a 95 % level of confidence, the null hypothesis that $\bar{x}$ and μ are the same cannot be rejected; that is, no significant systematic error has been demonstrated.

$$random\ uncertainty = \pm\frac{t_{crit}s}{\sqrt{n}} \qquad [1]$$

Since there are four replicate analyses, the degrees of freedom = n-1 = 4-1=3. Therefore, the $t_{critical}$ value (t) at *df*=3 is 3.18.

$$random\ uncertainty = \pm\frac{3.18\ x0.0033}{\sqrt{4}}$$

$$random\ uncertainty = \pm\frac{3.18\ x0.0033}{\sqrt{4}} = 0.0052_5$$

$$\text{Since } (\bar{x} - \mu) = 0.116 - 0.123 = -0.007$$

The difference of -0.007 is out of the range of random uncertainty *i.e.*, ± 0.0053, and therefore it means that the difference observed cannot be explained by the measurement uncertainties alone and is due to systematic error. It could also be said that the mean value of 0.116% does not demonstrate accuracy in terms of the certified value of 0.123% at a 95% level of confidence. At this level of confidence, we can state that 5 times out of 100, the mean can be expected to deviate by ± 0.0053 or more.

1.2.3 Example 3: Comparing a Mean and a Certified Value with stated measurement of uncertainty

In the example in 1.2.2, however, the measurement uncertainty of the certified value was not taken into consideration. The certificate of analysis states that the expanded measurement of uncertainty (*U*) is 0.01% at 95% level of confidence with a coverage factor *k*, of 2. Including the measurement of uncertainty will require the use of equation [2].

$$(\bar{x} - \mu) \le t_{crit}\sqrt{u_{\mu}^2 + \frac{s^2}{n}} \qquad [2]$$

Where, $(\bar{x} - \mu)$ is the difference of the mean of *n* replicates and the certified value, u_{μ} the standard uncertainty of the certified value, *i.e.*, *U/k*, *s* the standard deviation of n measurements and t_{crit} is the critical value for *n*-1 degrees of freedom.

$$-0.007 \leq 3.18\sqrt{0.005^2 + \frac{0.0033^2}{\sqrt{4}}}$$

$$-0.007 \leq 3.18\sqrt{0.000030445}$$

$$-0.007 \leq 0.0175$$

Since -0.0017 < 0.0175, there is no significant difference between the mean and the certified value taking into consideration stated measurement of uncertainty.

CITATION

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