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recommendation

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Measurement uncertainty and confidence intervals near natural limits

Analytical chemists often measure quantities close to the limits of the range in which the true value could possibly fall - the 'possible range'. Examples include measuring the purity of a material that is almost 100% pure, or measuring analytes that are present at concentrations close to zero. In such work, the usual expanded uncertainty interval ($x \pm U$) often extends beyond the possible range. Sometimes even individual measurements may lie out of that range. It is then unclear how best to report the result and associated uncertainty interval. There is a simple and statistically justifiable procedure for dealing with this situation when a statement about the true concentration of the analyte is required.

The problem of natural limits

For most chemical measurement, there are natural limits to the range in which the true value could possibly fall, the most obvious being that an analyte cannot be present at levels of above 100% or below zero. In alternative notation, this is a possible range of [0, 1]. (There may be other factors that reduce the possible range further, but for the present discussion we will assume that [0, 1] expresses the possible range.)

When both limits of an expanded uncertainty interval are within the possible range, the classical confidence interval is symmetric and performs well in terms of coverage. However, if the interval is large because of large experimental uncertainty or few degrees of freedol6S 161.94 298.63998 m161.94 299.23999 l161.94 301.03998 m161.94 301.63998 l161.94 303.44 m161.94 304.03998 l161.

tools.

Where the mean observation is also out of range, and we require the interval for the true concentration, the reported result should simply be shifted to the relevant limit (0 or 100%). Shifting to the limit does, however, lead to a small long-term bias, which may well be unacceptable to customers (or PT providers) demanding raw data for their own statistical analysis. These customers will continue to require the raw observations regardless of natural limits. Nonetheless, simple truncation at zero can be shown to provide minimal bias among the range of options so far examined for this situation.

If this procedure is followed, the expanded uncertainty interval becomes progressively more asymmetric as the result approaches the limit. Figure 2 illustrates the situation near zero, where the measured mean is reported until it hits zero, and is thereafter shifted to zero.

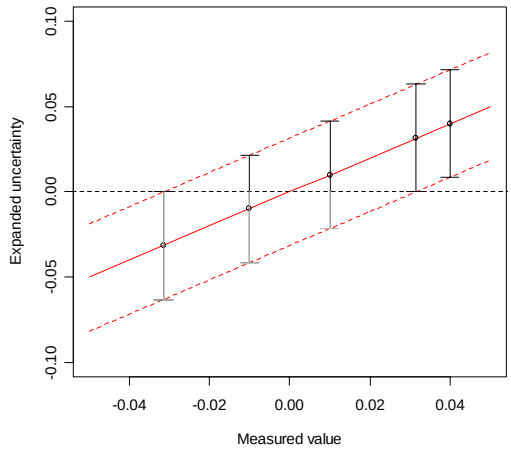

Figure 2. Truncating classical confidence intervals close to zero. The mean varies between -0.05 and 0.05, and the standard deviation is fixed at 0.01. The solid, partial bars show the reported uncertainty interval.

Eventually, the classical interval falls entirely beyond the natural limit, implying an adjusted interval of [0, 0]. This tells us that the results are inconsistent with any possible true concentration. The analyst should return to the original data and determine the cause. If this is impractical, or no cause can be found, the only recourse consistent with reporting an estimated true analyte concentration is to quote a value of zero with a large uncertainty. Preliminary studies suggest that a Bayesian maximum density interval based on the truncated *t*-distribution may be appropriate here. Unfortunately, this interval is not straightforward to calculate with ordinary analytical software or tables and has yet to be investigated fully for analytical chemistry applications. In the mean time, a conservative professional judgement is indicated; for example, basing the interval on a coverage factor of at least 3 instead of