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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 z

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.

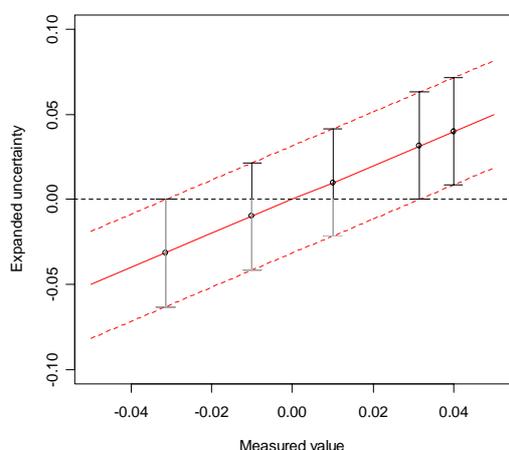


Figure 2. Truncating classical confidence intervals close to zero. The mean varies between -0.05 and 0.05, and the standard deviation is fixed at 0.01. The solid, partial bars show the reported uncertainty interval.

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