Estimation of Measurement Uncertainty

Two components (random and systematic bias) lead to the total uncertainty in analytical measurements. Rigorous error analysis calls for a) describing the mathematical function inclusive of all steps in the measurement process (e.g., taking aliquots, preparation and/or concentration steps, signal response calibration, etc.), b) measuring or otherwise determining the error (or error distribution) associated with each variable in the function and c) fully differentiating the function for each variable and calculating the total, propagated error. For complex, multi-step analytical methods generally employed in environmental laboratories, a completely rigorous evaluation of all errors is often impractical, especially considering the fact that sample matrix effects can contribute the greatest uncertainty to actual measurements on field samples.

An alternative means of estimating the total measurement error is to assess the results of measurements taken on known, traceable or certified standards carried through the entire analytical process. For quantitative laboratory measurements, statistical quality control measures are used within the Laboratory to estimate the uncertainty associated with analytical methods.

1) Method Startup – Whenever a new method is implemented or developed or when a new analytical technology is employed, it is the practice of the laboratory to initiate method validation exercises. Those exercises are intended to establish or verify method detection and quantitation limits and to establish or verify method performance expectations for accuracy and precision. The validation exercises are carried out over three separate days using independent preparation and analysis batches using a total of between 7 and 10 analytical samples taken through the entire method, including sample preparation steps. Until a larger data set can be accumulated and evaluated, statistical analysis of the method startup data is used to assess measurement uncertainty related to detection, accuracy and precision. Detection limits are established according to procedures referenced in the laboratory's quality manual; accuracy and precision are assessed using the process described under 'Ongoing Method Performance'. If method performance criteria are published and are demonstrated to be achievable by the laboratory, then method specified criteria for detection, accuracy and precision may be utilized instead of statistical metrics to assess analytical performance.
2) Ongoing Method Performance – Ongoing analytical performance is assessed, where applicable, from results of analytical measurements of certified reference materials or laboratory control samples (prepared from traceable standards when available), matrix spikes and replicate field samples. Performance data are compiled for each analytical batch and the data is accessed once a year. A minimum of two blanks, two-low-level (PQL) spikes and two laboratory control samples must be analyzed every quarter for all method/analyte/matrix combinations. Typically, a minimum of 8 - 20 data points (or a minimum of one year of data) is collected before assessment. If no method specified limits are published, statistical control limits are established and

used to assess method performance and analytical uncertainty (e.g., warning limits of ± 2 standard deviations and control limits of ± 3 standard deviations are employed). The Laboratory Information Management System (LIMS) quality control statistical tracking module allows managers to perform those assessments on the database of performance measurements. If method specified limits are published, those limits are used to assess ongoing analytical performance, however actual performance measurements are compiled to address client questions regarding uncertainty.

Reporting Uncertainty

The LIMS quality control manager module utilizes data tables containing quality control limits maintained by laboratory managers and provides for reported results to be linked to the analytical performance of quality control samples. Whenever quality control sample results fall outside expected statistical control limits (or outside method defined limits), excessive uncertainty due to sample matrix characteristics or faulty laboratory processes is assumed, and the associated sample results are automatically flagged accordingly on the final analysis report (using report QC comment flags and remark codes as defined in **SOP LB-027**). The final report advises clients to review associated quality control results to obtain estimates of uncertainty. For more in-depth inquires, clients may request a query of the laboratory's database to obtain analytical method performance statistics over time or for any selected time period.

The laboratory reports the results of performance check samples (precision and bias for laboratory control samples, matrix spikes and matrix spike duplicates) on its final analysis reports and in electronic data deliverables. From that information, clients may estimate uncertainty on a sample and/or batch specific basis. To the extent possible and where not constrained by method reporting requirements, the laboratory also uses significant figures reported for results to convey uncertainty. Further details regarding reporting of significant figures may be found in **SOP LB-024**.

References

1. SOP LB-024, *Significant Figures: Policy of the Florida DEP Laboratory*.
2. SOP LB-027, *Reporting Qualified Data and Correcting Quality Control Problems.*