

ESTIMATION OF ANALYTICAL MEASUREMENT UNCERTAINTY

TABLE OF CONTENTS	PAGE
SCOPE	3
REFERENCES	4
TERMINOLOGY	5
SUMMARY OF METHOD	9
PROCEDURE	12
CALCULATIONS	14
REPORT	23
PRECISION, BIAS, AND QUALITY CONTROL	23
APPENDIX A: GENERAL UNCERTAINTY BUDGET	29
APPENDIX B: EXAMPLE UNCERTAINTY BUDGET	26
APPENDIX C: EXAMPLE SPREADSHEET	28
APPENDIX D: SOFTWARE VALIDATION	31

1. SCOPE

- 1.1 This Standard Operating Procedure (SOP) describes the rationale and methodology for estimating analytical measurement uncertainty using the Quality Control-based Nested Approach for Estimating Analytical Measurement Uncertainty Spreadsheet. Other approaches that meet the requirements of ISO/IEC 170215 may also be used to estimate analytical measurement uncertainty.

- 1.2 This SOP applies to test methods that are within the scope of ISO/IEC 17025-1999 Standard: *General Requirements for the Competence of Testing and Calibration Laboratories* and it is based on the general rules outlined in *Guide to the Expression of Uncertainty in Measurement (GUM)*. The GUM approach is recommended in ISO/IEC 17025. (17025, 5.4.6.3 Note 3). According to ISO/IEC 17025, a laboratory “shall have and shall apply procedures for estimating uncertainty of measurement.” (17025, 5.4.6.2) and where appropriate, an estimation of uncertainty must be reported with the test result. (17025, 5.10.3.1c) This SOP is for use by environmental testing laboratories in the development and implementation of their quality systems. To be recognized as competent for carrying out specific environmental tests, this SOP describes the requirements that a laboratory must successfully demonstrate for the estimation of analytical measurement uncertainty.

- 1.3 When estimating analytical measurement uncertainty, all significant components of uncertainty must be identified and quantified. (17025, 5.4.6.3) Components that affect analytical measurement uncertainty include sampling, handling, transport, storage, preparation, and testing. (17025, 5.4.1) Components of uncertainty that do not contribute significantly to the total uncertainty of the test result can be neglected. (17025, 5.6.2.2.1)

- 1.4 Estimation of analytical measurement uncertainty is not required for qualitative tests with pass/fail or detect/non-detect results. However, decision uncertainty may be

required by estimating Type I and Type II errors. Certain biological tests, spot tests, and immunoassay tests are included in this category.

1.5 Estimation of analytical measurement uncertainty is not required for well-recognized quantitative test methods where the reference method specifies:

1.5.1 bias and precision acceptance limits,

1.5.2 form of presentation of the test result, and

1.5.3 procedure for estimating analytical measurement uncertainty

Certain methods with well-characterized uncertainties are included in this category (e.g., NIOSH 7400). (17025, 5.4.6.2 Note 2)

1.6 Estimation of analytical measurement uncertainty is required for quantitative test methods where the estimation of uncertainty is not specified in the method. The QC-based Nested Approach for Estimating Analytical Measurement Uncertainty Spreadsheet can be used to estimate analytical measurement uncertainty when Quality Control data is available. Certain performance-based methods (published regulatory or consensus methods) are included in this category.

2. REFERENCES

2.1 ISO 17025-1999, *General Requirements for the Competence of Testing and Calibration Laboratories*, The International Organization of Standardization (ISO) and the International Electrotechnical Commission (IEC), December 1999.

2.2 American National Standard for Expressing Uncertainty - U.S. Guide to the Expression of Uncertainty in Measurement, (US GUM), American National Standards Institute (ANSI) in 1997.

2.3 ISO Guide to the Expression of Uncertainty in Measurement (GUM), 1993.

- 2.4 Quality Assurance of Chemical Measurements, Taylor, John Keenan, Lewis Publishers, 1987.
- 2.5 *Environmental Analytical Measurement Uncertainty Estimation: Nested Hierarchical Approach*, Defense Technical Information Center #ADA396946, Ingersoll, William Stephen, 2001.
- 2.6 *QC-based Nested Approach for Estimating Measurement Uncertainty Spreadsheet*, Microsoft Excel Spreadsheet, Ingersoll, William Stephen, 2002.

3. TERMINOLOGY

- 3.1 Acceptance limits- data quality limits specified by the test method or generated by the laboratory.
- 3.2 Accuracy- the agreement of a single analytical measurement result to a reference value. Accuracy is a combination of random and systematic components. Random components affect the precision of the test result and systematic components affect the bias of the test result. See bias and precision.
- 3.3 “Backing-out”- the rearrangement of the “square root-of-the-sum-of-the-squares” equation to solve for an unknown component standard uncertainty.
- 3.4 Bias- the deviation of the mean of replicate analytical measurements from a reference analyte concentration. Relative bias is represented by analytical measurement mean minus the reference analyte concentration and the difference divided by the reference analyte concentration. See accuracy and precision.
- 3.5 Combined standard uncertainty- the standard uncertainty of the analytical measurement result that is the sum in quadrature (square-root-of-the-sum-of-the-squares) of the component standard uncertainties.

- 3.6 Coverage factor- the numerical factor used as a multiplier of the combined standard uncertainty to expand the uncertainty corresponding to a specific level of confidence. The Student's t -distribution is used for determining the coverage factor.
- 3.7 Duplicate samples- two samples taken from the same population and carried through certain stages of sampling and testing. Duplicate sample include field co-located duplicate samples, field-split duplicate samples, and laboratory duplicate subsamples.
- 3.8 Expanded uncertainty- the quantity defining an interval enveloping the analytical measurement that captures a large fraction of the distribution of analyte concentrations that could be attributable to the quantity measured. The combined standard uncertainty is multiplied by the coverage factor to calculate the expanded uncertainty.
- 3.9 Field samples- sampled and tested to represent the large-scale population distribution. Sampling usually includes primary sampling stage where the sample is extracted from the sample location and secondary sampling stage where the collected sample is reduced to a subsample after physical preparation such as milling and blending. Testing usually includes chemical preparation such as extraction and separation, and instrumental analysis.
- 3.10 Field co-located duplicate samples- samples collected near (0.5 to 3 feet) the field sample. Co-located duplicate samples are used to quantify the variance of the sampling strategy, sample collection, preparation, and testing stages.
- 3.11 Field-split duplicate sample- a field sample homogenized in the field and split into two or more portions that are sent to the laboratory as separate samples. Field-split duplicate samples are used to quantify the variance of the sample collection, preparation, and testing stages.

- 3.12 Hypothesis testing- the formulation of a decision such as not rejecting the null hypothesis, or rejecting the null hypothesis and accepting the alternative hypothesis. An example of hypothesis testing is that the null hypothesis (H_0) is $H_0 \geq$ the Action Level (AL) and the alternative hypothesis (H_A) is $H_A < AL$.
- 3.13 Independent Calibration Verification (ICV)- a standard solution used to verify the calibration curve derived from a source independent of the instrument calibration standard. The ICV is use to quantify second source standard variance and bias. Also called the Quality Control Sample.
- 3.14 Instrument Calibration Standard (ICS)- a reference material used to standardize an analytical instrument.
- 3.15 Instrument Performance Check (IPC)- the analyses of one of the ICSs to verified initial and continuing calibration. The IPC is used to quantify the instrumental testing repeatability variance and bias.
- 3.16 Laboratory control sample (LCS)- a clean-matrix reference material with an established analyte concentration derived from a source independent of the instrument calibration standard. The LCS is carried through the entire chemical preparation and testing procedures. The LCS is used to quantify the variance and bias of the chemical preparation and instrumental testing stages without matrix interference. Same a laboratory fortified blank. Also called a Laboratory fortified blank (LFB).
- 3.17 Laboratory duplicate subsample- a portion of the collected sample that is carried through the chemical preparation and testing. The Laboratory duplicate subsample is used to quantify the variance of the chemical preparation and instrumental testing stages with matrix interferences.
- 3.18 Matrix spiked sample- a subsample spiked with reference material with an established concentration derived from a source independent of the instrument calibration standard.

Matrix spiked sample are carried through the chemical preparation and testing stages. Matrix spiked samples are used to quantify the variance and bias of the chemical preparation and testing stages with matrix interference. Also called a Laboratory fortified matrix (LFM).

- 3.19 Precision- the dispersion of replicate analytical measurements. Precision is represented by the variance, relative variance, standard deviation, relative standard deviation, or range. See accuracy and bias.
- 3.20 QC-based Nested Approach Spreadsheet- the Microsoft Excel spreadsheet used to automatically calculate analytical measurement uncertainty.
- 3.21 Quality Assurance (QA)- the program used to establish confidence in the quality of data generated by the laboratory. Quality Control is a component of Quality Assurance.
- 3.22 Quality Control (QC)- the program that includes planning, implementing, monitoring, assessing, and adjusting processes that the laboratory uses to measure its capability and performance in generating quality data.
- 3.23 Quality Control Chart- a graph of analytical measurement results for a specific QC standard plotted sequentially with upper and lower control limits ($\pm 3\sigma$). A central line that is the best estimate of the average variable plotted, and upper and lower warning limits ($\pm 2\sigma$) are usually included in the Quality Control Chart.
- 3.24 Reference material- a traceable standard with an established analyte concentration.
- 3.25 Replicate analytical measurements- two or more results representing the same sample parameter. Replicate analytical measurements are used to quantify the analytical measurement repeatability precision.
- 3.26 Replicate samples- two or more samples representing the same population parameter.

- 3.27 Standard uncertainty- the analytical measurement uncertainty expressed as a standard deviation. The relative standard deviation represents the relative standard uncertainty.
- 3.28 Type I error- error that results in hypothesis testing for rejecting the null hypothesis when it should not be rejected.
- 3.29 Type II error- error that results in hypothesis testing for not rejecting the null hypothesis when it should be rejected.
- 3.30 Type A evaluation of uncertainty- the method of evaluation of uncertainty by the statistical analysis of a series of test results.
- 3.31 Type B evaluation of uncertainty- the method of evaluation of uncertainty by means other than statistical analysis.
- 3.32 Uncertainty- the parameter associated with the analytical measurement results that characterizes the dispersion of the values that could be reasonable attributed to the quantity measured.
- 3.33 Uncertainty interval- the range of analyte concentrations that an analytical measurement could represent at a specified level of confidence. The relative standard deviation is used to represent the relative standard uncertainty in the QC-based Nested Approach.

4. SUMMARY OF METHOD

- 4.1 The concept of analytical measurement uncertainty is widely recognized among analytical chemists. Replicate preparation and testing of a sample generates a range of results. This variability of results represents the analytical measurement uncertainty.

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- 4.2 This SOP includes requirements and information for assessing competence, and for determining compliance by the organization or accrediting authority granting the accreditation or approval. Accrediting authorities may use this SOP in assessing the competence of environmental laboratories.
- 4.3 If more stringent standards or requirements are included in a mandated test method or by regulation, the laboratory shall demonstrate that such requirements are met. If it is not clear which requirements are more stringent, the standard from the method or regulation must be followed.
- 4.4 Samples are routinely prepared and tested only once and replicate preparation and testing of environmental samples is not practical. However, any rigorous statistical determination of uncertainty based on a single test measurement is not possible. “There is no statistical basis for a confidence level statement of one measurement unless supported by a control chart or other evidence of statistical control.” (Taylor, J.K., 28).
- 4.5 The estimation of analytical measurement uncertainty is formalized in the *U.S. Guide to the Expression of Uncertainty in Measurement*, (US GUM), published by American National Standards Institute (ANSI) in 1997. The US GUM is the ANSI adoption of the *ISO Guide to the Expression of Uncertainty in Measurement* (GUM), published in 1993, and it establishes general rules to evaluate and express uncertainty for quantitative analytical measurements.
- 4.6 The general rules outline the process for identifying components of uncertainty, quantifying component standard uncertainty, combining standard uncertainties, expanding combined uncertainty, and reporting uncertainty.
- 4.7 The QC-based Nested Approach for Estimating Analytical Measurement Uncertainty Spreadsheet was developed to automate estimation of analytical measurement uncertainty.

- 4.8 Readily available laboratory Quality Control Chart data can be used to estimate the analytical measurement uncertainty for single test results. Using the laboratory generated Quality Control Limits, a mathematical model can be constructed to systematically “back-out” component uncertainties.
- 4.9 Laboratory-generated quality control data is used to populate a Microsoft Excel spreadsheet that automatically partitions sources of uncertainty, quantifies uncertainty for each component, and calculates the expanded uncertainty with optional bias correction. A histogram is generated to identify significant and negligible sources of uncertainty.
- 4.10 The steps for estimating uncertainty are incorporated into the following conceptual algorithm:
- 4.10.1 Specify the analyte of interest that is to be quantified
 - 4.10.2 Identify the sources of analytical measurement uncertainty
 - 4.10.3 Quantify the components of analytical measurement uncertainty
 - 4.10.4 Calculate the combined and expanded analytical measurement uncertainty
 - 4.10.4.1 The first step is to state what is to be quantified (the analyte of interest). A summary of the chemical preparation and testing methods is included.
 - 4.10.4.2 The second step is to identify the sources of analytical measurement variability or uncertainty. The sources of uncertainty can be partitioned into the following general components:
 - Large-scale site population variability
 - Small-scale sample location variability
 - Field sampling and laboratory subsampling variability
 - Sample chemical preparation variability
 - Sample test measurement variabilityAn Uncertainty Budget can be developed to tabulate analytical uncertainty.

4.10.4.3 The third step is to quantify the components of analytical measurement uncertainty. A frequent approach to evaluating and expressing uncertainty of a measurement is the use of the statistical concept of the confidence interval. The confidence interval is the range of results that reasonably captures the analyte concentration with a specified probability. When the confidence interval is constructed by the statistical analysis of replicate results, the approach is a Type A evaluation of standard uncertainty (US GUM, Section 4.2). When the confidence interval is not constructed by statistical analysis of replicate results, the approach is a Type B evaluation of standard uncertainty (US GUM, Section 4.3).

For statistical analysis (Type A evaluation), the standard deviation is calculated for the percent deviation (relative bias) for each quality control standard or sample. The standard deviation of analytical measurement results represents the standard uncertainty.

4.10.4.4 The fourth step is to combine the individual uncertainties and then apply a “coverage factor” which is chosen on the basis of the desired level of confidence to be associated with the interval around the measurement. Coverage factors are usually 2 or 3, corresponding to intervals with levels of confidence of approximately 95% and 99%, respectively.

5 PROCEDURE

- 5.1 If the reference method results in qualitative or semi-quantitative measurements, then the report result is an estimate and analytical measurement uncertainty is not quantified.
- 5.2 If the reference method specifies the procedure for estimation of analytical measurement uncertainty, then follow the reference method procedure.

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- 5.3 If the reference method does not specify the procedure for estimating analytical measurement uncertainty, then use this procedure.
- 5.4 The analytical measurement uncertainty for each quantitative field of testing must be estimated per analyte of interest, sample matrix, and analytical technology.
- 5.5 The automated calculation of laboratory analytical measurement uncertainty requires the following Quality Control standards:
 - 5.5.1 Instrument Calibration Standard or Instrument Performance Check
 - 5.5.2 Independent Calibration Verification or Quality Control Sample
 - 5.5.3 Laboratory Control Sample or Laboratory Fortified Blank
 - 5.5.4 Matrix Spiked Sample or Laboratory Fortified Matrix
- 5.6 Acquire twenty analyses for each of the QC standards described in Section 6.5. Twenty analyses are required for the automated calculation of analytical measurement uncertainty. These data may be acquired from Quality Control Charts.
- 5.7 Subtract the reference analyte concentration from the analytical measurement result and divide the difference by the reference analyte concentration.
- 5.8 Multiply relative error by 100 to calculate the percent deviation. The percent deviation is relative deviation from the reference analyte concentration multiplied by 100. Input the percent deviation data into the QC-based Nested Approach Spreadsheet in the appropriate column. See Appendix A for the mathematical algorithm used to calculate analytical measurement uncertainty.
- 5.9 Input the following information into the spreadsheet:
 - 5.9.1 Analyte, matrix, and technology
 - 5.9.2 Confidence level
 - 5.9.3 Analytical measurement
 - 5.9.4 Units

- 5.10 The confidence level is usually 95%, but other confidence levels can be selected according to client requirements. The QC-based Nested Approach Spreadsheet presents the confidence interval associated with the analytical measurement. Bias-correction is also presented for comparison. The bias-correction is based on the recovery efficiency of the laboratory chemical preparation and instrumental analysis components.
- 5.11 Representative sampling and subsampling eliminates sampling bias and imprecision associated materialization error.
- 5.12 The Uncertainty Budget of the general analytical measurement components of uncertainty can be tabulated from the QC-based Nested Approach Spreadsheet histogram. An example Uncertainty Budget is presented in Appendix B.
- 5.13 The Uncertainty Budget of specific analytical measurement components of uncertainty can be tabulated by itemizing sources of uncertainty that may or may not affect total analytical measurement uncertainty. An example Uncertainty Budget with specific sources of uncertainty is presented in Appendix C.
- 5.14 An example spreadsheet is presented in Appendix D with copper in wastewater by ICP quality control results.
- 5.15 The data from Appendix D is used in Appendix E to validate the QC-based calculator spreadsheet software.

6. CALCULATIONS

A.1 The mathematical model for uncertainty propagation is the Taylor series expansion.

A.1.1 The Equation A.1 is the Taylor series expansion for determining the estimated combined variance (u_c^2):

$$u_c^2(y) = \sum_{i=1}^n (\partial f / \partial x_i)^2 u^2(x_i) + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^n (\partial f / \partial x_i)(\partial f / \partial x_j) u(x_i, x_j)$$

Equation A.1

A.1.2 The Taylor series expansion equation can be simplified to calculate the combined standard uncertainty in Equation A.2:

$$u_c^2(y) = \sum_{i=1}^n [c_i u(x_i)]^2 + [c_2 u(x_2)]^2 + \dots + [c_n u(x_n)]^2 + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^n c_i c_j u(x_i) u(x_j) r_{ij}$$

Equation A.2

The symbol c_i represents $\partial f / \partial x_i$, symbol r_{ij} represents the correlation of x_i and x_j . The second term is the co-variance associated with x_i and x_j . The estimated co-variances or the estimated correlation coefficients are required if the variable x_i and x_j components are dependent. If the variable x_i and x_j are independent, then the co-variant term is equal to zero and the co-variant term drops out of the equation. The combined standard uncertainty estimate u_c uses the quadrature equation or “square-root-sum-of-squares” method for combining the standard uncertainties. This equation is the law of propagation of uncertainty.

A.1.3 There two primary approaches for applying the law of propagation of uncertainty: additive and multiplicative.

A.1.4 If y is an additive function of x_1, x_2, \dots, x_n , then Equation A.3 is used:

$$u_c(y) = \sqrt{[c_1 u(x_1)]^2 + [c_2 u(x_2)]^2 + \dots + [c_k u(x_n)]^2}$$

Equation A.3

A.1.5 If y is a multiplicative function of x_1, x_2, \dots, x_n , then Equation A.4 is used to determine the relative combined standard uncertainty $u_{c,r}$ where $y \neq 0$ and $|y|$ is the absolute value of y :

$$u_{c,r}(y) = [u_c(y)] / |y| = \sqrt{[c_1 u(x_1) / x_1]^2 + [c_2 u(x_2) / x_2]^2 + \dots + [c_k u(x_n) / x_n]^2}$$

Equation A.4

A.1.6 The QC-based Nested Approach Spreadsheet is based on multiplicative combination of component efficiencies; therefore Equation A.5 is used to estimate analytical measurement uncertainty.

A.2 The QC-based Nested Approach for Estimating Analytical Measurement Uncertainty is an automated system for calculating analytical measurement uncertainty.

- A.2.1 The data inputted into the Microsoft Excel QC-based Nested Approach Spreadsheet are the percent deviation of the Quality Control Chart data.
- A.2.2 The ICS, ICV, LCS, and MIS standards are used to calculate analytical measurement uncertainty for the laboratory.
- A.2.3 Calculate the percent deviation for ICS, ICV, LCS and MIS quality control data (that have a reference value) by equation A.5.1 and calculate the percent deviation for FDS and CLS quality control data (that don't have a reference value) by equation A.5.2.
- A.2.3.1 Calculate the percent deviation ($\%D_i$) for each individual ICS, ICV, LCS, and MIS result by subtracting the reference analyte concentration (T) from the each individual analytical measurement (X_i), dividing the difference by T , and multiplying the quotient by 100 in Equation A.5:

$$\%D_i = \left(\frac{(X_i - T)}{T} \right) * (100)$$

Equation A.5.1

- A.2.3.2 When data for field duplicate samples (FDS) and co-located duplicate samples (CLS) are available, calculate the percent deviation ($\%D_i$) or relative percent difference (RPD) for the FDS and the CLS by subtracting the second duplicate analytical measurement (X_2) from the first duplicate analytical measurement (X_1), dividing the difference by the average of the first and second duplicate samples, multiplying the quotient by 100, and taking the absolute value of the result in Equation A.6:

$$\%D_i = \left| \left(\frac{X_1 - X_2}{(X_1 + X_2)/2} \right) * \left(\frac{100}{1} \right) \right|$$

Equation A.5.2

- A.2.4 On page 1 input the $\%D$ of 20 Quality Control analytical measurements for the ICS, ICV, LCS, MIS, FDS, and CLS in the appropriate column of the spreadsheet.
- A.2.5 On page 1, when the data is inputted, the spreadsheet automatically calculates:
- Relative standard uncertainty (u_r) of the 20 (n) individual $\%D_i$ results

- Average bias ($\% \bar{B}$) based on the average ($\% \bar{D}$) of the n individual $\%D_i$ results
- Average recovery ($\% \bar{R}$) of the n individual $\%D_i$ results

The following equations are used to calculate:

- $\% \bar{B}$ in Equation A.6
- $\% \bar{R}$ in Equation A.7
- u_r in Equation A.8

$$\% \bar{B} = \% \bar{D} = \left(\frac{\%D_1 + \%D_2 + \dots + \%D_n}{n} \right)$$

Equation A.6

$$\% \bar{R} = (100 + \% \bar{D})$$

Equation A.7

$$u_r = \left(\frac{\sum_{i=1}^n (\%D_i - \% \bar{D})^2}{n-1} \right)^{1/2}$$

Equation A.8

A.2.6 On page 2, when the data is inputted, the spreadsheet automatically calculates standard uncertainty (s or u_r), recovery, and systematic error for components:

- IME – Intrinsic Measurement Effect
- SPE – Spike Preparation Effect
- PME – Preparation Method Effect
- MIE – Matrix Interference Effect
- SCE – Sample Collection Effect
- SLE – Sample Location Effect

A.2.7 The relative standard deviation of the Instrumental Calibration Standard (ICS) represents the uncertainty associated with instrumental repeatability Intrinsic Measurement Effects (IME) in Equation A.9.

$$ICS u_r = IME u_r$$

Equation A.9

A.2.8 The relative standard deviation of the Independent Calibration Verification (ICV) is a combination of IME and the Spike Preparation Effects (SPE) in Equation A.10.

$$ICV \mathbf{u}_r = \sqrt{(IME \mathbf{u}_r)^2 + (SPE \mathbf{u}_r)^2}$$

Equation A.10

Equation A.10 is rearranged to “back-out” the SPE standard uncertainty from the known ICV and IME standard uncertainties:

$$SPE \mathbf{u}_r = \sqrt{(ICV \mathbf{u}_r)^2 - (IME \mathbf{u}_r)^2}$$

A.2.9 The relative standard deviation of the Laboratory Control Sample (LCS) is a combination of IME, SPE, and the Preparation Method Effects (PME) in Equation A.11.

$$LCS \mathbf{u}_r = \sqrt{(IME \mathbf{u}_r)^2 + (SPE \mathbf{u}_r)^2 + (PME \mathbf{u}_r)^2}$$

Equation A.11

Equation A.11 is rearranged to “back-out” the PME standard uncertainty from the known ICV, IME, and SPE standard uncertainties:

$$PME \mathbf{u}_r = \sqrt{(LCS \mathbf{u}_r)^2 - ((IME \mathbf{u}_r)^2 + (SPE \mathbf{u}_r)^2)}$$

A.2.10 The relative standard deviation of the Matrix Spiked Sample (MIS) is a combination of IME, SPE, PME, and the Matrix Interference Effects (MIE) in Equation A.12.

$$MIS \mathbf{u}_r = \sqrt{(IME \mathbf{u}_r)^2 + (SPE \mathbf{u}_r)^2 + (PME \mathbf{u}_r)^2 + (MIE \mathbf{u}_r)^2}$$

Equation A.12

Equation A.12 is rearranged to “back-out” the MIE standard uncertainty from the known MIS, IME, SPE, and PME standard uncertainties:

$$MIE \mathbf{u}_r = \sqrt{(MIS \mathbf{u}_r)^2 - ((IME \mathbf{u}_r)^2 + (SPE \mathbf{u}_r)^2 + (PME \mathbf{u}_r)^2)}$$

A.2.11 The relative standard deviation of the Field-split Duplicate Sample (FSR) is a combination of IME, PME, MIE, and the Sample Collection and Subsampling Effects (SCE) in Equation A.13.

$$FSR \mathbf{u}_r = \sqrt{(IME \mathbf{u}_r)^2 + (SCE \mathbf{u}_r)^2 + (PME \mathbf{u}_r)^2 + (MIE \mathbf{u}_r)^2}$$

Equation A.13

Equation A.13 is rearranged to “back-out” the MIE standard uncertainty from the known FSR, IME, PME, and MIE standard uncertainties:

$$SCE \mathbf{u}_r = \sqrt{(FSR \mathbf{u}_r)^2 - ((IME \mathbf{u}_r)^2 + (PME \mathbf{u}_r)^2 + (MIE \mathbf{u}_r)^2)}$$

A.2.12 The relative standard deviation of the Field Co-located Duplicate Sample (CLR) is a combination of IME, PME, MIE, SCE, and the small-scale Sample Location Effects (SLE) in Equation A.14.

$$CLR \mathbf{u}_r = \sqrt{(IME \mathbf{u}_r)^2 + (SCE \mathbf{u}_r)^2 + (PME \mathbf{u}_r)^2 + (MIE \mathbf{u}_r)^2 + (SLE \mathbf{u}_r)^2}$$

Equation A.14

Equation A.14 is rearranged to “back-out” the SLE standard uncertainty from the known CLR, IME, PME, MIE and SCE standard uncertainties:

$$SLE \mathbf{u}_r = \sqrt{(CLR \mathbf{u}_r)^2 - ((IME \mathbf{u}_r)^2 + (PME \mathbf{u}_r)^2 + (MIE \mathbf{u}_r)^2 + (SCE \mathbf{u}_r)^2)}$$

A.2.13 The large-scale natural variability of the analyte distribution inherent in the sampling site is not measured directly, but is derived by a process of sampling and testing. This process confounds the natural site population parameter mean and standard deviation. The relative standard deviation of the collection of Site Field Samples (SFS) is a combination of IME, PME, MIE, SCE, SLE, and the large-scale Sampling Site Effects (SSE) in Equation A.15.

$$SFS \mathbf{u}_r = \sqrt{(IME \mathbf{u}_r)^2 + (SCE \mathbf{u}_r)^2 + (PME \mathbf{u}_r)^2 + (MIE \mathbf{u}_r)^2 + (SLE \mathbf{u}_r)^2 + (SSE \mathbf{u}_r)^2}$$

Equation A.15

Equation A.15 is rearranged to “back-out” the SSE standard uncertainty from the known SFS, IME, PME, MIE, SCE, and SLE standard uncertainties:

$$SSE \mathbf{u}_r = \sqrt{(SFS \mathbf{u}_r)^2 - ((IME \mathbf{u}_r)^2 + (PME \mathbf{u}_r)^2 + (MIE \mathbf{u}_r)^2 + (SCE \mathbf{u}_r)^2 + (SLE \mathbf{u}_r)^2)}$$

A.2.14 The spreadsheet has a logic test to make the calculations more robust. If a component in the logic hierarchy has a standard uncertainty less than the standard uncertainty of a component lower in the logic hierarchy, then the spreadsheet reports zero for the higher component.

A.2.15 The component recovery ($\% \bar{R}_{IME}$) for IME is calculated by using Equation A.16.

$$\% \bar{R}_{IME} = 100 + \% \bar{D}_{ICS}$$

Equation A.16

A.2.16 The component recovery ($\% \bar{R}_{SPE}$) for SPE is calculated by using Equation A.17.

$$\% \bar{R}_{SPE} = \left(\frac{(100 + \% \bar{D}_{ICV})}{(\% \bar{R}_{IME} / 100)} \right)$$

Equation A.17

A.2.17 The component recovery ($\% \bar{R}_{PME}$) for PME is calculated by using Equation A.18.

$$\% \bar{R}_{PME} = \left(\frac{(100 + \% \bar{D}_{LCS})}{(\% \bar{R}_{IME} / 100)(\% \bar{R}_{SPE} / 100)} \right)$$

Equation A.18

A.2.18 The component recovery ($\% \bar{R}_{MIE}$) for MIE is calculated by using Equation A.19.

$$\% \bar{R}_{MIE} = \left(\frac{(100 + \% \bar{D}_{LCS})}{(\% \bar{R}_{IME} / 100)(\% \bar{R}_{SPE} / 100)(\% \bar{R}_{PME} / 100)} \right)$$

Equation A.19

A.2.19 The component systematic error ($\% \bar{B}_{IME}$) for IME is calculated by using Equation A.20.

$$\% \bar{B}_{IME} = (\% \bar{R}_{IME} - 100)$$

Equation A.20

A.2.20 The component systematic error ($\% \bar{B}_{SPE}$) for SPE is calculated by using Equation A.21.

$$\% \bar{B}_{SPE} = (\% \bar{R}_{SPE} - 100)$$

Equation A.21

A.2.21 The component systematic error ($\% \bar{B}_{PME}$) for PME is calculated by using Equation A.22.

$$\% \bar{B}_{PME} = (\% \bar{R}_{PME} - 100)$$

Equation A.22

A.2.22 The component systematic error ($\% \bar{B}_{MIE}$) for MIE is calculated by using Equation A.23.

$$\% \bar{B}_{MIE} = (\% \bar{R}_{MIE} - 100)$$

Equation A.23

A.2.23 The analyst must select from the menu and input the percent confidence. The following table (Table A.1) is a list of available confidence levels with corresponding coverage factors based on 20 analytical measurements.

TABLE A.1: CONFIDENCE LEVELS AND COVERAGE FACTORS

Confidence Level (Percent Confidence)	Two-Tailed Distribution Coverage Factor (Student's t-Value for 19 Degrees of Freedom)
80	1.328
90	1.729
95	2.093
99	2.861

A.2.24 After selection of the confidence level, the spreadsheet automatically presents the coverage factor and calculates the Relative Analytical Measurement Uncertainty and the Relative Systematic Error.

A.2.25 The combining relative standard uncertainty in percent for routine single test measurements (${}^{RST}u_r$) is a combination of IME, PME, and MIE in Equation A.24.

$${}^{RST}u_r = \sqrt{(IME u_r)^2 + (PME u_r)^2 + (MIE u_r)^2}$$

Equation A.24

A.2.26 The combined standard uncertainty is expanded to the specified confidence level by multiplying the ${}^{RST}u_r$ by the appropriate coverage factor.

A.2.27 The combined relative bias in percent for the routine single test measurements ($\% \bar{B}_{RST}$) is a combination of IME, PME, and MIE in Equation A.25.

$$\% \bar{B}_{RST} = 100 * ((\% \bar{R}_{IME} / 100) (\% \bar{R}_{PME} / 100) (\% \bar{R}_{MIE} / 100)) - 1)$$

Equation A.25

A.2.28 On page 3 the analyst must enter the analytical measurement and the units of the analytical measurement.

A.2.29 The spreadsheet automatically calculates and presents the uncertainty interval expanded to the specified level of confidence for the test result. The calculation of the confidence interval (CI) for the analytical measurement result (C_m) is presented in Equation A.26.

$$CI = C_m \pm (C_m) * (k * {}^{RST}u_r)$$

Equation A.26

A.2.30 The spreadsheet automatically calculates and presents the bias corrected results (C_{mBC}) and the bias-corrected confidence interval (CI_{BC}) expanded to the specified confidence level for the test result in Equations A.27a and A.27b.

$$C_{mBC} = \left(\frac{C_m}{\left(\frac{100 + \%B_{RST}}{100} \right)} \right)$$

Equation A.27a

$$CI_{BC} = C_{mBC} \pm (C_{mBC}) * (k * {}^{RST}u_r)$$

Equation A.27b

7. REPORT

7.1 Documentation of a analytical measurement may require the following:

- 7.1.1 Description of the methods used to calculate the measurement result and estimation of analytical measurement uncertainty
- 7.1.2 Uncertainty Budget of uncertainty components
- 7.1.3 Correction factors used to normalize (correct for bias) the data
- 7.1.4 Report the analytical measurement result with estimated expanded uncertainty and the level of confidence

8 PRECISION, BIAS, AND QUALITY CONTROL

- 8.1 The estimation of analytical measurement is an integral component of the Quality Assurance-Quality Control system. “One of the prime objectives of quality assurance is to evaluate measurement uncertainty.” (Taylor, J.K., 10)
- 8.2 A component of Quality Control is laboratory generated Quality Control Charts. The use of the QC-based Nested Approach Spreadsheet is based on the bias and precision limits of Quality Control Charts.
- 8.3 Quality Control Charts must represent the laboratory’s capability and performance, and the analytical measurement system must have a stable pattern of variation. “Until a measurement operation has attained a state of statistical control, it cannot be regarded in any logical sense as measuring anything at all.” (Taylor, J.K., 13)
- 8.4 The QC-based estimation of analytical measurement uncertainty per analyte, matrix, and technology must be calculated when Quality Control Charts are updated. Usually Quality Control Charts are updated annually or when there is a major change in primary analytical personnel, analytical instrumentation, or analytical procedures.
- 8.5 Though it is recognized that other sources of uncertainty contribute to total analytical measurement uncertainty, the laboratory is usually only responsible for reporting estimations of uncertainty for the analysis components of the laboratory. If the laboratory has access to field-split duplicates data or field co-located duplicate data, then sample collection and subsampling, and sampling strategy components can be quantified.
- 8.6 Each analyst is responsible for calculating estimations of uncertainty and Quality Control assessment of the reasonableness of the calculations. The automated Microsoft Excel spreadsheet (QC-based Nested Approach for Estimating Analytical Measurement Uncertainty) calculates the analytical measurement uncertainty based on Quality Control Chart data.

8.7 The person responsible for Quality Assurance must review analytical measurement uncertainty calculations at least annually. The estimation of analytical measurement uncertainty must be uniform and consistent to ensure data quality and data comparability

APPENDIX A: GENERAL UNCERTAINTY BUDGET

The general components of sampling and testing that are sources of analytical measurement uncertainty are tabulated in the following table (Table A-1).

TABLE A-1: SOURCES OF UNCERTAINTY

Uncertainty Sources	Source Symbol	Analytical Sample	Analytical Sample Symbol
Intrinsic (Instrumental) Measurement Effects	IME	Instrument Calibration Standard	ICS
Spike Preparation Effects	SPE	Initial Calibration Verification Standard	ICV
Preparation Method Effects	PME	Laboratory Control Sample	LCS
Matrix Interference Effects	MIE	Matrix Interference Sample Matrix Spike/ Duplicate Sample	MIS MS/MSD
Sample Collection Effects	SCE	Field Replicate (Duplicate) Sample (Collected from same location and during same sampling event time)	FSR

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Sample Location Effects	SLE	Co-Located (Same Location) Sample (Collected 0.5 – 3 feet away from field sample)	CLR
Sampling Site Population Effects	SSE	Site field sample collected from the environmental site for the study	SFS

An example of general uncertainty budget components of sampling and testing that contribute the analytical measurement are presented in the follow table (Table A-2).

TABLE A-2: GENERAL UNCERTAINTY BUDGET

Component	Symbol	Relative Standard Uncertainty	Probability Distribution	Sensitivity Coefficient	Relative Uncertainty Contribution
Intrinsic Instrumental Measurement Effects	IME	2%	Normal	1	1
Laboratory Preparation Method Effects	PME	4%	Normal	1	2
Sample Matrix Interference Effects	MIE	6%	Normal or Lognormal	1	3
Sample Collection and Subsampling Effects	SCE	8%	Normal or Lognormal	1	4
Sampling Strategy Effects	SSE	9%	Normal or Lognormal	1	4.5
Sampling Site Media Contamination Effects	SME	14%	Normal or Lognormal	1	7

APPENDIX B: EXAMPLE UNCERTAINTY BUDGET FOR METHOD 3050B

Uncertainty Source	Uncertainty Interval (99.7% CL)	Evaluation Type	Distribution
Weighing-Boat Weight (Top Loader Balance)	5 +/-0.05 g	Type A	Normal
Sample Weight Wet (Tared) (Top Loader Balance)	996 +/-10 g	Type A	Normal
Drying Temperature (Thermometer)	30 +/-4 ° C	Type B	U-shaped
Drying Time (Analog Clock)	24 +/- 2 hours	Type B	Rectangular
Particle Size Reduction - #10 sieve 2 mm (Milling Machine)	1+/- 1 mm	Type B	Triangular
Homogenization (Tumbler Blending Machine)	30+/-2 rpm	Type B	Triangular
Tumbler Time (Analog Clock)	18+/-2 hours	Type B	Rectangular
Weight of the Dried Sample + Boat Dry (Top Loader Balance)	664 +/- 7 g	Type A	Normal
Weighing-Boat Weight (Analytical Balance)	1+/-0.001 g	Type A	Normal
Weight of the Subsample (Tared)	2+/-0.002 g	Type A	Normal

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(Analytical Balance)			
Quantitative Transfer Efficiency (From Weighing-Boat to Beaker)	99+/-1%	Type B	Triangular
Spike Volume (Eppendorf Pipette)	0.5 +/- 0.005 mL	Type A	Normal
Spike Concentration (Manufacture's Reagent Purity)	995 +/- 10 mg/L	Type B	Rectangular
Hot-Plate/Hot-Block/Microwave Digestion Temperature (Thermometer)	95 +/-5 ° C	Type B	U-shaped
Extraction Time (Analog Clock)	4.75+/-0.25 hours	Type B	Rectangular
Nitric Acid Volume (Transfer Pipette)	10 +/- 1 mL	Type B	Triangular
Nitric Acid Concentration (Manufacture's Reagent Purity)	69.5 +/- 0.5 %	Type B	Rectangular
Hydrogen Peroxide Volume (Transfer Pipette)	10+/-3 mL	Type B	Triangular
Hydrogen Peroxide Concentration (Manufacture's Reagent Purity)	30.5+/-1.5%	Type B	Rectangular
Hydrochloric Acid Volume (Transfer Pipette)	10+/-1 mL	Type B	Triangular
Hydrochloric Acid Concentration (Manufacture's Reagent Purity)	36.5+/-0.5%	Type B	Rectangular
Extraction Efficiency (Matrix Interference)	96+/-2%	Type B	Triangular
Quantitative Transfer Efficiency (From Beaker to Graduated Cylinder)	99.5+/-0.5%	Type B	Triangular
Dilution Volume (Graduated Cylinder)	100+/-3 mL	Type A	Normal

EXPLANTIONS OF DISTRIBUTIONS FOR METHOD 3050B

Normal Distribution

The normal distribution is usually determined statistically. The normal distribution is based on the central limit theorem where random sampling results in a normal distribution of data regardless of the underlying distribution of the quantity measured.

$$S = a/3 \text{ or approximately } 0.33 a$$

Where S is the standard deviation and a is $\frac{1}{2}$ the range of values.

Triangular Distribution

The triangular is more conservative than normal. The triangular is used when the variation limits are known (lowest and highest), and it is known that it is a better probability (most likely) of finding values close to the mean value that further away from it.

$$S = a/(6)^{0.5} \text{ or approximately } 0.41 a$$

Rectangular Distribution

Rectangular is more conservative than the triangular. The upper and lower bounds of range of data is estimated, but the distribution is not known so all results are assumed to be equally likely. For example, the throw of a dice has a rectangular distribution. 1, 2, 3, 4, 5, and 6 are equally likely and the probability is 1/6 or 0.167 that 1 to 6 will occur. There is a zero probability that <1 or >6 will occur. It is often used when information is derived from calibration certificates and manufacturer's specifications.

$$S = a/(3)^{0.5} \text{ or approximately } 0.58 a$$

U-shaped Distribution (Sine Wave)

U-shaped is more conservative than rectangular and the U-shaped returns a higher equivalent standard deviation value for the same variation width, +/- a. U-shaped distribution is not as rare as it seems. Cyclic events, such as temperature of a hot plate, oven, or furnace, often yield uncertainty contributors that fall into this sine-wave pattern. Another example is the power cycle of a microwave digestion system. If we assume that the amplitude of the signal is sinusoidal, the distribution for incident voltage is the U-shaped distribution. There is a better probability of finding values close to the variation limits than around the mean value.

$$S = a/(2)^{0.5} \text{ or approximately } 0.71 a$$

APPENDIX C: QC-BASED NESTED APPROACH FOR ESTIMATING ANALYTICAL MEASUREMENT UNCERTAINTY EXAMPLE SPREADSHEET

C-1: Page 1

- C1.1 The analyte of interest, sample matrix, and analytical technology is entered as “Copper in Wastewater by ICP”.
- C1.2 For the ICS, ICV, LCS, and MIS, 20 replicate analytical measurement results are entered.

QC-based Nested Approach for Estimating Analytical Measurement Uncertainty					Page 1	
<i>What are the analyte, matrix, and technology?</i>					Copper in Wastewater by ICP	
Enter 20 replicate results for the following quality control samples as relative deviation (%):						
ICS - Instrument calibration standard						
ICV - Second source calibration verification standard						
LCS - Laboratory control sample						
MIS - Matrix interference sample (matrix spike, organic surrogate, radiochemical tracer)						
FDS - Field-split duplicate sample						
CLS - Co-located duplicate sample						
	ICS	ICV	LCS	MIS	FDS	CLS
	1.1	0.5	4.0	12.0	0.0	0.0
	0.8	0.1	0.5	1.4	0.0	0.0
	0.4	1.0	1.5	8.0	0.0	0.0
	2.0	1.2	1.7	3.7	0.0	0.0
	1.0	0.2	0.1	12.0	0.0	0.0
	1.2	0.4	2.2	0.4	0.0	0.0
	1.7	1.2	0.4	3.6	0.0	0.0
	3.7	0.9	0.3	0.1	0.0	0.0
	1.1	0.1	0.5	2.7	0.0	0.0
	3.1	1.3	15.0	17.0	0.0	0.0
	2.0	0.9	20.0	30.0	0.0	0.0
	0.7	1.0	0.4	3.7	0.0	0.0
	0.4	2.0	4.0	1.5	0.0	0.0
	0.9	0.2	0.6	5.0	0.0	0.0
	1.4	1.0	1.5	1.4	0.0	0.0
	1.9	1.4	5.0	20.0	0.0	0.0
	2.0	1.5	24.0	3.5	0.0	0.0
	1.5	1.7	3.0	5.0	0.0	0.0
	1.6	3.0	13.0	-24.0	0.0	0.0
	1.1	3.1	11.0	-13.0	0.0	0.0
Std. Dev.	0.84	0.85	7.2	11.1	0.0	0.0
Bias	1.5	1.1	5.4	4.7		
Recovery	101.5	101.1	105.4	104.7		

C-2: Page 2

C-2.1 The confidence level is selected from: 80%, 90%, 95%, and 99%.

C-2.2 The confidence level is entered as “95”.

QC-based Nested Approach	Copper in Wastewater by ICP	Page 2																								
<p>Components of Analytical Uncertainty IME - Intrinsic instrumental measurement effects SPE - Spike preparation effects PME - Preparation method effects MIE - Matrix interference effects SCE - Sample collection effects SLE - Sample location effects</p>																										
<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th colspan="2">Component Percent Standard Uncertainty</th> </tr> </thead> <tbody> <tr> <td>IME ~ 0.8</td> <td>% relative standard deviation</td> </tr> <tr> <td>SPE ~ 0.1</td> <td>% relative standard deviation</td> </tr> <tr> <td>PME ~ 7.1</td> <td>% relative standard deviation</td> </tr> <tr> <td>MIE ~ 8.5</td> <td>% relative standard deviation</td> </tr> <tr> <td>SCE ~ 0.0</td> <td>% relative standard deviation</td> </tr> <tr> <td>SLE ~ 0.0</td> <td>% relative standard deviation</td> </tr> </tbody> </table>	Component Percent Standard Uncertainty		IME ~ 0.8	% relative standard deviation	SPE ~ 0.1	% relative standard deviation	PME ~ 7.1	% relative standard deviation	MIE ~ 8.5	% relative standard deviation	SCE ~ 0.0	% relative standard deviation	SLE ~ 0.0	% relative standard deviation	<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th>Component Percent Recovery</th> <th>Component Systematic Error</th> </tr> </thead> <tbody> <tr> <td>IME ~ 101</td> <td>IME ~ 1 percent</td> </tr> <tr> <td>SPE ~ 100</td> <td>SPE ~ 0 percent</td> </tr> <tr> <td>PME ~ 104</td> <td>PME ~ 4 percent</td> </tr> <tr> <td>MIE ~ 99</td> <td>MIE ~ -1 percent</td> </tr> </tbody> </table>	Component Percent Recovery	Component Systematic Error	IME ~ 101	IME ~ 1 percent	SPE ~ 100	SPE ~ 0 percent	PME ~ 104	PME ~ 4 percent	MIE ~ 99	MIE ~ -1 percent	
Component Percent Standard Uncertainty																										
IME ~ 0.8	% relative standard deviation																									
SPE ~ 0.1	% relative standard deviation																									
PME ~ 7.1	% relative standard deviation																									
MIE ~ 8.5	% relative standard deviation																									
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IME ~ 101	IME ~ 1 percent																									
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MIE ~ 99	MIE ~ -1 percent																									
		2.093																								
		2.093																								
		2.093																								
		WRONG CL																								
		WRONG CL																								
<p><i>What is the Confidence Level (CL)? Enter ONLY one of these percentages: 80, 90, 95, 99</i></p>		<input style="width: 50px;" type="text" value="95"/> %																								
<p>Your specified t-value is <input style="width: 50px;" type="text" value="2.093"/> for a Two-Tailed Normal Distribution Confidence Interval</p>																										
<p>Relative Analytical Measurement Uncertainty for routine field samples (Only the IME, PME, and MIE are combined for the analytical measurement uncertainty)</p>																										
<input style="width: 150px;" type="text" value="23.3"/> % relative uncertainty																										
<p>Relative Systematic Error associated with the measurement of routine field samples (Only the IME, PME, and MIE biases are combined for the analytical measurement systematic error)</p>																										
<input style="width: 150px;" type="text" value="5.1"/> % relative systematic error																										

C-3: Page 3

C-3.1 The analytical measurement result is entered as “10”.

C-3.2 The units are entered as “mg/L”.

QC-based Nested Approach
Copper in Wastewater by ICP
Page 3

Partitioning of Uncertainty

Component	Percent Relative Uncertainty (%)
IME	~0.8
SPE	~0.1
PME	~7.1
MIE	~8.5
SCE	0.0
SLE	0.0

What is the analytical measurement result?

What are the analytical measurement units?

If the sample measurement is **10 mg/L** ,
then the uncertainty interval is **7.7 - 12.3 mg/L** at the **95 % Confidence Level (Expanded Uncertainty)**

For the above result, if the systematic measurement error (bias) is corrected, and
the corrected measurement is **9.5 mg/L** ,
then the uncertainty interval is **7.3 - 11.7 mg/L** at the **95 % Confidence Level (Expanded Uncertainty)**

APPENDIX D: SOFTWARE VALIDATION BASED ON DATA IN APPENDIX C

Replicate Number	ICS			ICV		
	%D	%D-% \bar{D}	(%D-% \bar{D}) ²	%D	%D-% \bar{D}	(%D-% \bar{D}) ²
1	1.1	-0.4	0.14	0.5	-0.6	0.40
2	0.8	-0.7	0.52	0.1	-1.0	1.07
3	0.4	-1.1	1.25	1.0	-0.1	0.02
4	2.0	0.6	0.31	1.2	0.1	0.00
5	1.0	-0.5	0.24	0.2	-0.9	0.87
6	1.2	-0.3	0.07	0.4	-0.7	0.54
7	1.7	0.3	0.07	1.2	0.1	0.00
8	3.7	2.3	5.06	0.9	-0.2	0.06
9	1.1	-0.4	0.18	0.1	-1.0	1.07
10	3.1	1.6	2.63	1.3	0.2	0.03
11	2.0	0.5	0.27	0.9	-0.2	0.06
12	0.7	-0.8	0.61	1.0	-0.1	0.02
13	0.4	-1.1	1.17	2.0	0.9	0.75
14	0.9	-0.6	0.34	0.2	-0.9	0.87
15	1.4	-0.1	0.01	1.0	-0.1	0.02
16	1.9	0.4	0.18	1.4	0.3	0.07
17	2.0	0.5	0.27	1.5	0.4	0.13
18	1.5	0.0	0.00	1.7	0.6	0.32
19	1.6	0.1	0.01	3.0	1.9	3.48
20	1.1	-0.4	0.14	3.1	2.0	3.86

Equation A.6 **ICS**

$$\% \bar{D} = \left(\frac{\%D_1 + \%D_2 + \dots + \%D_n}{n} \right)$$

$$\% \bar{D} = 12.7/20 = 1.5\%$$

Equation A.7 $\% \bar{R} = (100 + \% \bar{D}) = 100 + 1.5 = 101.5\%$

Equation A.8 $u_r = \left(\frac{\sum_{i=1}^n (\%D_i - \% \bar{D})^2}{1} \right) = 13.47$

$$u_r = \left(\frac{\sum_{i=1}^n (\%D_i - \% \bar{D})^2}{n-1} \right) = 0.71$$

$$u_r = \left(\frac{\sum_{i=1}^n (\%D_i - \% \bar{D})^2}{n-1} \right)^{1/2} = 0.84\%$$

ICV

$$\% \bar{D} = \left(\frac{\%D_1 + \%D_2 + \dots + \%D_n}{n} \right)$$

$$\% \bar{D} = 32.6/20 = 1.1\%$$

$\% \bar{R} = (100 + \% \bar{D}) = 100 + 1.1 = 101.1\%$

$$u_r = \left(\frac{\sum_{i=1}^n (\%D_i - \% \bar{D})^2}{1} \right) = 13.65$$

$$u_r = \left(\frac{\sum_{i=1}^n (\%D_i - \% \bar{D})^2}{n-1} \right) = 0.72$$

$$u_r = \left(\frac{\sum_{i=1}^n (\%D_i - \% \bar{D})^2}{n-1} \right)^{1/2} = 0.85\%$$

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Replicate Number	LCS			MIS		
	%D	%D - % \bar{D}	(%D - % \bar{D}) ²	%D	%D - % \bar{D}	(%D - % \bar{D}) ²
1	4.0	-1.4	2.06	12.0	7.3	53.29
2	0.5	-4.9	24.35	1.4	-3.3	10.89
3	1.5	-3.9	15.48	8.0	3.3	10.89
4	1.7	-3.7	13.95	3.7	-1.0	1.00
5	0.1	-5.3	28.46	12.0	7.3	53.29
6	2.2	-3.2	10.47	0.4	-4.3	18.49
7	0.4	-5.0	25.35	3.6	-1.1	1.21
8	0.3	-5.1	26.37	0.1	-4.6	21.16
9	0.5	-4.9	24.35	2.7	-2.0	4.00
10	15.0	9.6	91.49	17.0	12.3	151.29
11	20.0	14.6	212.14	30.0	25.3	640.09
12	0.4	-5.0	25.35	3.7	-1.0	1.00
13	4.0	-1.4	2.06	1.5	-3.2	10.24
14	0.6	-4.8	23.38	5.0	0.3	0.09
15	1.5	-3.9	15.48	1.4	-3.3	10.89
16	5.0	-0.4	0.19	20.0	15.3	234.09
17	24.0	18.6	344.66	3.5	-1.2	1.44
18	3.0	-2.4	5.93	5.0	0.3	0.09
19	13.0	7.6	57.23	-24.0	-28.7	823.69
20	11.0	5.6	30.97	-13.0	-17.7	313.29

Equation A.6 **LCS**

$$\% \bar{D} = \left(\frac{\%D_1 + \%D_2 + \dots + \%D_n}{n} \right)$$

MIS

$$\% \bar{D} = \left(\frac{\%D_1 + \%D_2 + \dots + \%D_n}{n} \right)$$

Equation A.7

$$\% \bar{D} = 12.7/20 = 5.4\%$$

$$\% \bar{R} = (100 + \% \bar{D}) = 100 + 5.4 = 105.4\%$$

$$\% \bar{D} = 32.6/20 = 4.7\%$$

$$\% \bar{R} = (100 + \% \bar{D}) = 100 + 4.7 = 104.7\%$$

Equation A.8

$$u_r = \left(\frac{\sum_{i=1}^n (\%D_i - \% \bar{D})^2}{n-1} \right)^{1/2} = 979.73$$

$$u_r = \left(\frac{\sum_{i=1}^n (\%D_i - \% \bar{D})^2}{n-1} \right)^{1/2} = 2360.42$$

$$u_r = \left(\frac{\sum_{i=1}^n (\%D_i - \% \bar{D})^2}{n-1} \right)^{1/2} = 51.56$$

$$u_r = \left(\frac{\sum_{i=1}^n (\%D_i - \% \bar{D})^2}{n-1} \right)^{1/2} = 124.23$$

$$u_r = \left(\frac{\sum_{i=1}^n (\%D_i - \% \bar{D})^2}{n-1} \right)^{1/2} = 7.18\%$$

$$u_r = \left(\frac{\sum_{i=1}^n (\%D_i - \% \bar{D})^2}{n-1} \right)^{1/2} = 11.14\%$$

$$ICS_{u_r} = IME_{u_r} = 0.84\%$$

Equation A.9

If $ICS_{u_r} \geq ICV_{u_r}$, then SPE_{u_r} is estimated as zero, else:

$$SPE_{u_r} = \sqrt{(ICV_{u_r})^2 - (IME_{u_r})^2} = \sqrt{0.85^2 - 0.84^2} = 0.10\%$$

Equation A.10

If $ICV_{u_r} \geq LCS_{u_r}$, then PME_{u_r} is estimated as zero, else:

$$PME_{u_r} = \sqrt{(LCS_{u_r})^2 - ((IME_{u_r})^2 + (SPE_{u_r})^2)} = \sqrt{7.2^2 - (0.84^2 + 0.10^2)} = 7.1\%$$

Equation A.11

If $LCS_{u_r} \geq MIS_{u_r}$, then MIE_{u_r} is estimated as zero, else:

$$MIE_{u_r} = \sqrt{(MIS_{u_r})^2 - ((IME_{u_r})^2 + (SPE_{u_r})^2 + (PME_{u_r})^2)} = \sqrt{11.1^2 - (0.84^2 + 0.10^2 + 7.1^2)} = 8.5\%$$

Equation A.12

$$\% \bar{R}_{IME} = 100 + \% \bar{D}_{ICS} = 100 + 1.5 = 101.5\%$$

Equation A.16

$$\% \bar{R}_{SPE} = \left(\frac{(100 + \% \bar{D}_{ICV})}{(\% \bar{R}_{IME} / 100)} \right) = \frac{(100 + 1.1)}{(101.5 / 100)} = 99.7\%$$

Equation A.17

$$\% \bar{R}_{PME} = \left(\frac{(100 + \% \bar{D}_{LCS})}{(\% \bar{R}_{IME} / 100)(\% \bar{R}_{SPE} / 100)} \right) = \frac{(100 + 5.4)}{(101.5 / 100)(99.7 / 100)} = 104.3\%$$

Equation A.18

$$\% \bar{R}_{MIE} = \left(\frac{(100 + \% \bar{D}_{MIS})}{(\% \bar{R}_{IME} / 100)(\% \bar{R}_{SPE} / 100)(\% \bar{R}_{PME} / 100)} \right) = \frac{(100 + 4.7)}{(101.5 / 100)(99.7 / 100)(104.3 / 100)} = 99.3\%$$

Equation A.19

$$\% \bar{B}_{IME} = (\% \bar{R}_{IME} - 100) = (101.5 - 100) = 1.5\%$$

Equation A.20

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$$\% \bar{B}_{SPE} = (\% \bar{R}_{SPE} - 100) = (100 - 100) = -0.3\%$$

Equation A.21

$$\% \bar{B}_{PME} = (\% \bar{R}_{PME} - 100) = (104 - 100) = 4.3\%$$

Equation A.22

$$\% \bar{B}_{MIE} = (\% \bar{R}_{MIE} - 100) = 99 - 100 = -0.7\%$$

Equation A.23

$$RST \mathbf{u}_r = \sqrt{(IME \mathbf{u}_r)^2 + (PME \mathbf{u}_r)^2 + (MIE \mathbf{u}_r)^2} = \sqrt{0.84^2 + 7.18^2 + 11.14^2} = 11.13\%$$

Equation A.24

$$\% \bar{B}_{RST} = 100 * ((\% \bar{R}_{IME} / 100) (\% \bar{R}_{PME} / 100) (\% \bar{R}_{MIE} / 100)) - 1)$$

$$\% \bar{B}_{RST} = 100 * ((101.5 / 100) (104.3 / 100) (99.3 / 100)) - 1) = 5.1\%$$

Equation A.25

$$CI = C_m \pm (C_m) * (k * RST \mathbf{u}_r) = 10 \pm (10 * 2.093 * 0.1113) = 10 \pm 2.3 \text{ mg/L}$$

Equation A.26

$$C_{mBC} = \left(\frac{C_m}{\left(\frac{100 + \% \bar{B}_{RST}}{100} \right)} \right) = \frac{10}{\left(\frac{100 + 5.1}{100} \right)} = 9.5 \text{ mg / L}$$

Equation A.27a

$$CI_{BC} = C_{mBC} \pm (C_{mBC}) * (k * RST \mathbf{u}_r) = 9.5 \pm (9.5 * 2.093 * 0.1113) = 9.5 \pm 2.2 \text{ mg/L}$$

Equation A.27b