ENVIRONMENTAL ANALYTICAL MEASUREMENT UNCERTAINTY ESTIMATION

NESTED HIERARCHICAL APPROACH

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Chapter 1: Introduction

This document provides guidance for estimating environmental analytical measurement uncertainty. Each year billions of dollars are expended to generate environmental study data. These data are used in programs to protect the environment and mitigate environmental impacts. The quality of these data affect environmental cleanup, compliance, and ambient monitoring decision-making. To provide data of known quality, sampling and analysis plans are developed to accurately and precisely represent the contaminant distribution parameters of an environmental site or population. Associated with the environmental study data is the estimated measurement uncertainty that results from the sampling and analysis process. This measurement uncertainty affects environmental study data quality. The process of making decisions under uncertainty is a challenge for environmental decision-makers. Decision-makers must assess the effects of measurement uncertainty on environmental decisions. While the possibility of a decision error can never be totally eliminated, it can be controlled. To control decision errors, the measurement uncertainty must be controlled.

The inherent population variability and the measurement uncertainty associated with the sampling and analysis process cause environmental study data uncertainty. Inherent population variability is the temporal and spatial heterogeneity of a contaminant distributed throughout an environmental population. Sampling and analysis process uncertainty results from variability in the location, collection, subsampling, preparation, and testing of samples. The nested hierarchical approach to estimating analytical measurement uncertainty is used to identify the sources of analytical variability and determine their contribution to measurement uncertainty. Because a measurement is derived from the sampling and analysis process, the uncertainty associated with each analytical phase contributes to the measurement uncertainty. The analytical phases include:

- Sample location
- Sample collection
- Sample reduction (subsampling)
- Sample preparation
- Sample testing

The nested hierarchical approach is based on the "American National Standard for Expressing Uncertainty – U.S. Guide to the Expression of Uncertainty in Measurement" (GUM). The GUM provides general rules for evaluating and expressing measurement uncertainty. The GUM model includes the following four steps:

- Evaluate the components of the analytical process that contribute to uncertainty
- Examine the co-variances of the components of uncertainty
- Estimate the uncertainties
- Expand the uncertainty

The nested hierarchical approach uses backward induction to "back-out" component uncertainties from quality control sample data. The approach uses the statistical quality control limits data generated by each laboratory to evaluate and estimate measurement uncertainty. Using quality control data, the sources of variation that affect measurement uncertainty can be broken down into specific components. By working backward from the estimated uncertainty of quality control samples to estimate component uncertainties, the environmental laboratory can estimate component uncertainties and combined significant components to estimate single test measurement uncertainty of routine environmental field samples.

Chapter 2: Rationale of the Nested Approach

In 1977, the international metrology community began addressing the lack of consensus on the expression of measurement uncertainty. The importance of an internationally accepted procedure for expressing measurement uncertainty and for combining individual uncertainty components into a total uncertainty was recognized. The International Organization of Standardization (ISO/IEC 17025) standard for the general requirements for competence of testing and calibration laboratories requires that testing laboratories estimate measurement uncertainty. Without the uncertainty statement, the test result is of unknown quality and cannot be compared with action levels for reliable environmental decision-making.

In 1993, the "Guide to the Expression of Uncertainty in Measurement" (GUM) was published by the International Organization of Standardization (ISO) in collaboration with the seven member Joint Committee for Guides on Metrology (JCGM). This approach was developed by the International Committee for Weights and Measures (CIPM) and was presented in the GUM. The "American National Standard for Expressing Uncertainty-U.S. Guide to the Expression of Uncertainty in Measurement" (GUM) is the American National Standards Institute (ANSI) adoption of the ISO GUM. The ANSI adoption of the ISO GUM provides the mathematical model and general rules for the nested approach to estimating measurement uncertainty.

The GUM introduced a formal definition of uncertainty, distinguished uncertainty from error, and described the steps for evaluating uncertainty. Measurement error is attributable to systematic effects and measurement uncertainty is attributed to random effects. The GUM model is a systematic approach to evaluating uncertainty. The GUM incorporates the following general rules for evaluating and expressing measurement uncertainty:

- Systematic errors are corrected to a reference value, and measurement uncertainty is the standard uncertainty of the correction or standard deviation of the population mean.
- If a reference value is not available to correct for systematic effects, then error corrections are not made and the standard uncertainty assessment is made from standard deviation of the sample mean**.**
- Standard uncertainty of an analytical component is represented as the standard deviation of the component.
- Standard uncertainty is assumed to be normally distributed with symmetrical intervals centered on the mean.
- The quadrature equation, or square root of the sum of the squares, is used to combine standard uncertainties.
- Multiplicative components are combined as relative combined standard uncertainty, $u_{c,r}$**,** while additive components are combined as combined standard uncertainty, u_c.
- Expanded uncertainty**,** U or relative expanded uncertainty, U_r**,** is determined from a Student's t-distribution table for the scalar factor, k**,** that is multiplied with the combined standard uncertainty, u_c or relative combined standard uncertainty, $u_{c,r}$ for expanded uncertainty, U or relative expanded standard uncertainty, U_r**.**

The nested approach works within the GUM framework by providing detailed and specific instructions for evaluating and estimating measurement uncertainty from quality control data. Standard uncertainties are derived from laboratory quality control limits data standard deviations. The nested approach "backs-out" the component standard deviations or standard

uncertainties, normalizes the measurement result to correct for systematic error, and integrates the relative variances of components to estimate uncertainty of a single test measurement.

The standard uncertainty, $u(x_i)$, is evaluated for each component, x_i, of the measurement equation $y = f(x_1, x_2, \ldots x_n)$ where y is the measurement result and is a function of the measurement component independent variables $x_1, x_2, \ldots x_n$. Each uncertainty component, x_i, is represented by an estimated standard deviation, s_i, and the estimated standard deviation represents the standard uncertainty, u_i.

The sample analyte recovery is a multiplicative combination of the component recoveries of the analytical process. Because the combination of components is multiplicative, the relative standard deviation is used to estimate the relative standard uncertainty. The relative standard uncertainty of each component, x_i, is the standard uncertainty divided by the measurement result, or $u(x_i)/y$. The relative combined standard uncertainty, $u_{c,r}$, is a mathematical combination of component relative standard uncertainties. The relative combined standard uncertainty is the combined standard uncertainty, u_c, divided by the measurement result, y, or $u_c(y)/y$ and is equal to $u_{c,r}$.

The estimated uncertainties are combined by a first-order Taylor series approximation of the measurement equation $y = f(x_1, x_2, \ldots x_n)$. The combined standard uncertainty, $u_c(y)$, of the measurement result y is the square root of the estimated combined variance $u_c^2(y)$. For additive functions, the propagation of uncertainty is calculated for the combined uncertainty as the square root of the sum of the squares. This is the "law of propagation of uncertainty." The "propagation of uncertainty" is possible because variances are additive properties while standard deviations are not. If y is an additive function of $x_1, x_2, \ldots x_n$, then the following equation is used to combine standard uncertainties.

$$(u_c(y))^2 = \sum_{i=1}^{n} u(x_i)^2$$

Equation 2.1

If y is a multiplicative function of $x_1, x_2, \ldots x_n$, then the following equation is used to determine the relative combined standard uncertainty $u_{c,r}$ where $y \neq 0$ and $|y|$ is the absolute value of y:

$$(u_c(y)/|y|)^2 = \sum_{i=1}^{n} (u(x_i)/x_i)^2$$

Equation 2.2

Derivations of these equations are found in Appendix D.

The contaminant distribution parameters of the average and variability of the contaminant concentration of the population are estimated by the statistical mean (***X-bar***) and standard deviation ($s_{X\text{-}bar}$) derived from the environmental study data. The population average is characterized by the mean (μ) and the variability is characterized by the standard deviation (σ). These population parameters can only be estimated. The environmental population is analyzed by breaking down the site into a limited number of sample locations because it is impractical to measure every point of a population. The sample location represents a portion of the environmental population. Only a portion of the sample location is actually collected as a sample and only a portion or subsample of the collected sample is actually prepared and tested.

Because measurements are estimates of the environmental parameters, there is always uncertainty associated with the environmental study data. As stated earlier, total study uncertainty is a combination of the inherent population variability of the study contaminant and the measurement uncertainty. The measurement uncertainty is a combination of the uncertainty derived from the sampling strategy, field sample collection, and laboratory preparation and testing. Each tier of the analytical process increases the total study uncertainty. The hierarchy of total study uncertainty is presented in Appendix B.

Analytical uncertainty is sometimes applied exclusively to intrinsic instrumental measurement repeatability. However, analytical uncertainty is usually broadened to include the uncertainty associated with the physical and chemical procedures used to prepare the sample for instrumental analysis. The term "analyze" means to break down into parts and analytical measurement uncertainty is generalized in this document to include the uncertainty associated with the field and laboratory sampling and analysis used to generate data.

The environmental analytical process is a system of component sub-processes. The components of the analytical process include sampling strategy, sample collection, sample preparation, and instrumental analysis. The components affect the uncertainty of the analytical measurement. The multi-tiered process of where, when, and how the samples were located, collected, subsampled, prepared, and tested affect measurement results. For the nested approach, the variances of the components are evaluated and the standard deviation attributable to each component is used as the standard uncertainty of each component. The component uncertainties are combined and expanded to represent the estimated measurement uncertainty at a specific confidence level.

Study population variability is the natural variability inherent in the contaminant distribution of the sampling site media. This underlying variability cannot be reduced, but it can be estimated. There may be a wide range in contaminant concentration variability in a study population that is caused by complex spatial and temporal distributions. Heterogeneous soil and rock media, complex hydrogeologic conditions, contaminant stratification, and geochemical fate and transport processes contribute to the inherent variability of the study population contaminant concentration.

In field sampling and laboratory analysis plans, a limited number of samples are collected and tested to capture and characterize study population central tendency and variability. Field sampling includes the number, location, collection, and preservation of the samples. Laboratory analysis includes the subsampling, preparation and test measurement or determination of the samples. Sampling design uncertainty results because only a limited number of the possible locations within the study population are actually sampled and tested. Sample collection uncertainty is affected by the process of obtaining representative samples of a subset of the study population. The subsampling, extraction, separation, concentration, and testing procedures affect laboratory preparation and test determination variability. Selecting certain sampling and analysis strategies and methods reduces the uncertainty associated with measurement results.

The sampling frame selection and sampling unit definition as well as the sampling strategy model selected affect sampling design uncertainty. Sampling design uncertainty occurs because the sampling strategy does not capture the complete extent of the inherent or natural variability that exists in the population. The number and location of the samples affect the degree of sample representativeness for the study population inherent variability. As the density of samples increase the sampling design uncertainty decreases. Random, unclustered, and uncorrelated samples increase the accuracy of the estimated average contaminant concentration.

When samples are not random, unclustered, and uncorrelated, geostatistical evaluation must be applied so that bias can be controlled.

The sample collection personnel competency, sample volume or mass collected, and sampling equipment collector efficiency affect sample collection uncertainty. During sampling events cross contamination between samples, sample preservation, and analyte degradation also affect sample collection uncertainty.

Physical and chemical preparation processes affect preparation uncertainty. Physical preparation includes sample homogenization, particle size reduction, and subsampling. Chemical preparation includes extraction, separation, and concentration. Each tier of the preparation process affects the percent recovery of the analyte. Matrix interferences affect both preparation and test determination. Refractory matrices inhibit extraction of the analytes while co-precipitation of interferents inhibits during analyte recovery concentration and separation procedures. Co-elution of interferents (during instrumental determination) affects method selectivity while carryover from high concentration samples affect following samples test determinations. Instrumental fluctuation affects intrinsic measurement repeatability and contributes to irreducible measurement uncertainty.

Chapter 3: Methodology

The nested approach to estimate measurement uncertainty uses a systematic process to quantify the standard uncertainties of the analytical process components. The system of components that are sources of sample measurement uncertainty a combination of field sampling and laboratory measurement activities. Figure 3.1 is a simplified "fish-bone" diagram that represents the components of sample measurement uncertainty. The "cause-and-effect" approach is an inductive process of working from the particular effects to the general effect. The particular effects of the component uncertainties combine to **cause** the general **effect** of sample uncertainty in Figure 3.1.

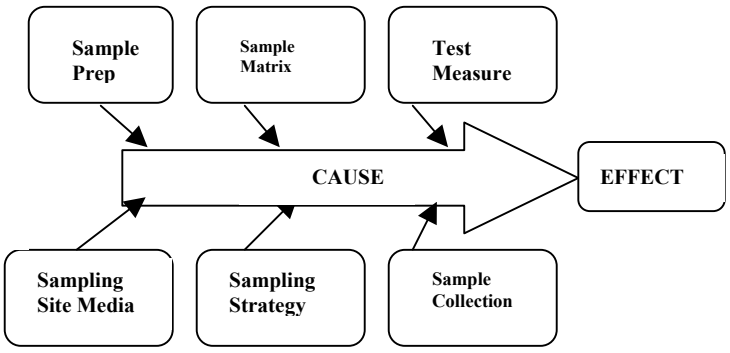


Figure 3.1 Environmental Field Sample Uncertainty Diagram

For the nested approach, the estimation process uses backward induction. The component uncertainties are estimated from quality control sample data standard deviations. The process of estimation is counter current to the cause-and-effect diagram. With backward induction, the relative combined standard uncertainty is used to derive the component relative standard uncertainty. The relative combined standard uncertainty is estimated from the quality control sample or standard. The relative standard uncertainties of the components are "backed-out" of the quadrature equation. Each component variability compounds the uncertainty of the measurement results.

The nested approach provides the mechanism for separating the estimated uncertainty attributable to field sampling activities from the estimated uncertainty attributable to laboratory measurement activities. However, when data is not available from field-splits and co-located samples, only the uncertainty attributable to laboratory measurement activities can be estimated. The laboratory can assign the measurement uncertainty associated with a single test measurement of a sample using instrument calibration standard, independent calibration verification standard, laboratory control sample, and matrix interference sample. If the project has additional QC samples such as field-splits or co-located samples, then this additional data can be used to better estimate the uncertainty associated with field sampling activities.

Using the nested approach enables the environmental analytical laboratories and data users to identify the components of uncertainty, estimate the uncertainty associated with each component, and evaluate the proportionate contribution of uncertainty of the components to the routine field sample uncertainty. With the nested approach, uncertainty from field sampling activities and lab measurement activities can be partitioned from of the total study uncertainty. This can provide the data user information concerning how to adjust the analytical process. For example, if 80% of the measurement uncertainty were attributable to field activities, spending

additional funds on laboratory measurement activities to reduce analytical uncertainty would be unsuccessful. Identification of "weak links" in the hierarchy of components that contribute to total study uncertainty may indicate that definitive sampling and analysis methods do not significantly decrease the total study uncertainty because of the underlying heterogeneity of the media. The total study uncertainty can be assumed to be representative of the inherent population variability when the measurement uncertainty attributable to the sampling and analysis process is less than 1/3 of the inherent population variability.

For example, if the total study uncertainty estimated from the relative standard deviation of routine samples is 31.6%, and the measurement uncertainty is estimated to be 10.0%, then the inherent population variability (represented by a relative standard deviation) is 30.0%. The ratio of measurement uncertainty to inherent population variability is 1:3. The following equations demonstrate the nested approach and the technique of backward induction.

$$u_{rT}^{\,2} = u_{rP}^{\,2} + u_{rM}^{\,2}$$

Equation 3.1

The term $u_{rT}^{\,2}$ is the total study relative uncertainty squared, $u_{rP}^{\,2}$ is the population relative variability squared and $u_{rM}^{\,2}$ is the measurement relative uncertainty squared. The term u_T can be replaced with 31.6% and the term u_M can be replaced with 10%. The equation is rearranged to "back-out" the unknown u_{rP}.

$$u_{rP}^{\,2} = (31.6\%)^2 - (10.0\%)^2$$

Equation 3.2

$$u_{rP}^{\,2} = 1000 - 100$$

The square root of the variance is taken to determine the relative standard deviation or relative standard uncertainty.

$$u_{rP} = 30.0\%$$

For this example, the contribution from the sampling and analysis uncertainty to the total study uncertainty in insignificant. Theoretically, if we could get rid of the contribution of the sampling and analysis uncertainty from the total study uncertainty, the total study uncertainty would be 30% instead of 31.6%. The resulting decrease of the total study uncertainty would be about 5%. The procedures for partitioning and estimating the components of measurement uncertainty are explained in Appendices C and E.

Sampling design planning is the initial phase in the sample measurement process. Sampling plans are developed with the strategic goal of capturing representative samples of the site that approximate the distribution of environmental contamination. Sampling strategies include determining the number and location of samples, as well as suitable sampling, preservation, and handling techniques. Selection of the appropriate sampling strategy requires estimation of the uncertainty associated with the field activities and the uncertainty associated with the laboratory activities. Sampling site spatial or temporal variability is analyzed by simple statistical calculations or by more complex geostatistical approaches. Field activity uncertainty sources include temporal and spatial contamination level variation, sample-handling variation during collection, and site media variation.

Sampling strategies include stratified random sampling, systematic grid sampling, composite sampling, and "hot-spot" sampling. Some characteristics of the inherent or natural population variability are not captured because of limited sampling. Because the spatial distribution of contaminants at environmental sites are variable, sampling and analysis plans must be designed to collect enough samples to ensure that "hot-spot" contamination are detected. Composite sampling is preformed to estimate the average contaminant concentrations at a reduced laboratory analytical cost. However, compositing can result in underestimating the tails of contaminant concentration distributions and mask "hot-spot" contamination. Stratified random sampling requires division of the site into sampling areas or strata. Strata include soil matrices such as sand, silt, clay, or loam. Strata can also include materials such as ash or concrete rubble. The stratified random sampling approach assumes that each individual stratum is more internally homogenous than the site as a whole. Grouping similar sampling points together and randomly sampling each group separately minimize the variation within each sample group. The mean and standard deviation of the measurement from each stratum can be used to compare with different strata or combined for a composite result of the entire site.

The systematic grid sampling approach describes sample collection at predetermined systematic intervals in a grid pattern. This strategy ensures complete coverage of a large site, which minimizes sampling uncertainty. "Hot-spot" sampling applies to a site with a history of small, localized areas with high levels of contamination, or "hot-spots." Along with the routine field samples quality control samples are collected. The kinds of quality control samples that are collected include background, co-located replicate samples, field-split replicate samples, equipment blanks, trip blanks, and field blanks.

Because blank samples should be below the quantitation limit and therefore the accuracy and precision cannot be determined, these samples are not incorporated into the estimation of measurement uncertainty. However, the co-located replicate samples and the field-split replicate samples are designed to assess the random and systematic variation of the sample collection process and evaluate the efficacy of the sampling strategy. Field-split samples are collected from one location, homogenized on-site, divided into separate containers, and handled as separate samples throughout the sample process. The field-split replicate samples assess sampling point heterogeneity, sample collection methods, laboratory preparation methods, and laboratory instrumental analysis methods. Field homogenization of field/field-split samples affects the distribution of the contaminant dispersed throughout the sample matrix. Inappropriate homogenization would result in a different average distribution in the individual duplicate samples. One duplicate could represent 75% recovery of the average contamination while the other duplicate could represent 125% recovery of the average contamination. Inappropriate sieving could also bias the percent recovery of the contaminant.

The co-located replicate sample is collected from 0.5 to 3 feet away from the sampling point as a selected field sample. It is within the same sample location area, but not at the identical sample location point. The interval between the co-located sample and the original sample is smaller than the interval between samples. Co-located replicate samples assess the spatial and temporal variations at the sample location area in addition to sample collection, field preparation, handling, and transportation procedures, and instrumental analysis precision. Variation between co-located replicate samples is used to evaluate the efficacy of the sampling strategy. Co-located samples could indicate that a different sampling strategy should be used to capture the distribution of contaminants at the environmental site.

Sampling equipment can affect the recovery of the contaminant analytes of interest. A sample should be collected with equipment constructed of materials that are compatible with the sample matrix and that do not interfere with recovery of the analyte. Bias can be introduced when the sampling equipment absorbs or leaches the analyte of interest. The mobility of the analyte can also affect the recovery of the contaminant. For example, volatile contaminants migrate into void spaces of samples. Volatile contaminants can be biased by aeration or mixing of sample materials, elevated temperature, and exposure of a sampled matrix to air. Analyte recovery may also be affected by sample preservation. Proportional error could be associated with inappropriate preservation activities if a certain percentage of the analyte precipitates or reacts because of inappropriate preservation. These field uncertainties would be compounded in the analysis process.

Uncertainty sources from laboratory activities include: sample homogenization variation from inadequate milling, blending, or stratification as well as precipitation of solids; variation in analyte extraction, concentration, and separation during sample chemical preparation and instrumental analysis variation (such as calibration and standardization problems). Samples are organized into preparation batches that consist of field samples, matrix spike and matrix spike duplicate samples, laboratory control samples and method blank samples. Matrix spike samples are used to assess matrix interference, method preparation performance, and method instrument performance. The laboratory control sample is used to assess method preparation performance and method instrument performance only. The samples analyzed by the laboratory also include instrument calibration samples, initial and continuing calibration verification samples, replicate samples, and customer samples.

The recovery of the analyte of interest is determined for each of the quality control samples that have a traceable concentration of the analyte. Standards with the analytes of interest and instrumental interferents are analyzed. Laboratory control sample are spiked with the analytes of interest and processed through the preparation method. The matrix spike and matrix spike duplicates are subsamples of a customer sample that are spiked and processed through the sample preparation method.

Quality control and routine samples that laboratories analyze have uncertainty associated with the sample measurement. This uncertainty results from the instrumental analysis process, the sample preparation process, the sample collection process, and the inherent heterogeneity of the contaminant dispersion throughout the sampling site. Processing samples affects the accuracy and precision of recovery for the analytes measured. Each processing level increases the uncertainty associated with the measurement.

The data used in the nested hierarchical approach is based on statistical quality control data. Control charts are established for quality control samples with quantifiable accuracy and precision limits. Laboratories incorporate quality control samples into physical and chemical preparation batches, and instrumental analysis batches. The quality control samples are charted to assess the laboratory's measurement quality and include the following:

- Calibration standards.
- Independent source calibration verification standards.
- Continuing calibration verification standards.
- Laboratory control samples.
- Matrix recovery samples.

Laboratory quality control standards and samples have uncertainty associated with the measurement. The intrinsic measurement uncertainty can be estimated from the quantification of

the instrument calibration standard (ICS). The instrument is standardized with a certified standard of known analyte concentration. After standardization, the analyte concentration of the instrument calibration standard is measured. Because the ICS is reanalyzed immediately after standardization, deviations from the certified value are the result of the intrinsic instrumental measurement effects. The independent, source calibration verification standard (ICV) is a certified reference from a different standards vendor or from the same standards vendor, but a different preparation lot. This standard is an independent, second source for calibration verification. The ICV incorporates the intrinsic measurement uncertainty and the uncertainty associated with the standard preparation. This would include the vendor preparation and testing uncertainty and the environmental laboratory preparation uncertainty such as transfer and dilution of the certified standard to make up stock solutions.

The laboratory control sample (LCS) is an analyte-free and interferent-free matrix sample that is spiked with a working standard traceable to a certified standard, and are prepared and tested with a batch of routine environmental samples. The LCS uncertainty includes the intrinsic measurement uncertainty, the spike preparation uncertainty, and the method preparation uncertainty. The method preparation uncertainty includes uncertainties associated with extraction, concentration, and separation of the analytes of interest.

The matrix interference sample (MIS) is a subsample of a routine sample spiked with a working standard traceable to a certified standard, and prepared and tested with a batch of routine samples. In addition to the intrinsic, spike preparation, and method preparation uncertainties, the MIS also has the uncertainty associated with matrix effects or interferences.

Chapter 4: Comments of the Validity of the Assumptions

The nested approach uses the square root sum of squares or sum in quadrature equation for estimating measurement uncertainty. The sum in quadrature uncertainty equation is simplified by making certain reasonable assumptions, and the nested approach uses historical relative standard deviations of quality control samples to represent relative combined standard uncertainties. These combined standard uncertainties are used to estimate the component standard uncertainties. The following assumptions serve as a basis for simplifying the uncertainty estimation using the nested approach:

1. The data from the quality control samples are normally distributed.
2. The mutually exclusive analytical process components are statistically independent.
3. The uncertainty intervals of the components are proportional to analyte concentration and relative uncertainty is constant.
4. The sources of uncertainty from the analytical process are multiplicatively combined to calculate sample measurement uncertainty.
5. The uncertainty of sample results is a collectively exhaustive combination of component uncertainties that are combined by fractional quadratic summation.

Assumption 1: Normal Distribution

The data from the quality control samples are normally distributed. This assumption is valid because of the central limit theorem. When an adequate number of samples are taken from any population distribution, the measurements approach a normal distribution. Statistical evaluation of quality control samples confirms this assumption. From 20 to 30 quality control sample measurements charted on a frequency plot approach a bell shaped dispersion of the measurement results.

For an assumed normal distribution, the uncertainty interval, $\pm U$, is equal to $\pm k u_c$ where k is the covering factor and u_c is the combination of the uncertainty component standard deviations, s, of a large number of replicate analyses. Measurement uncertainty contains the actual measurement uncertainty with a stated level of confidence. The standard deviation, σ, times the covering factor, k associated with the level of confidence is used to calculate uncertainty.

Because the measurement population standard deviation, σ, is not known, but can be estimated from the sample measurement standard deviation, s, the covering factor, k, is based on the Student's t-distribution, not the normal z-distribution. The estimated sample measurement standard deviation, s, must be calculated from repetitive measurements. The combined measurement standard deviation times the covering factor, k, associated with the level of confidence is used to calculate uncertainty. Therefore, measurement uncertainty contains the combined standard uncertainty with a stated level of confidence.

The t-distribution is applicable to a small number of measurements. As the number of degrees of freedom increase to infinity, ∞, the t- distribution approaches the normal distribution. At 100 measurements, the t-variate is approximately 2 at the 95% confidence level at 100 measurement results. Therefore, the t- distribution approximates the normal distribution. For the uncertainty interval derived from the typical laboratory control chart limits of between 20 to 30 measurements, the Student's t-value for k should be used.

Random scatter of results is inherent in any measurement process. Random data are dispersed in a probabilistic pattern and vary in sign (±) and magnitude, but with a significantly large number of replicate measurements, random variation averages out to approximately zero. For sample sizes greater than 30, the standard deviation estimate approaches that for an infinitely large number of replicates. Fewer measurements inevitably give estimates that underestimate inherent precision of the method, and when the sample size is less than 7, the probable uncertainty in the estimation is too great for control limits based on it to be useful.

The central tendency and the dispersion statistics summarize the normal distribution. For environmental measurement of contaminants, the central tendency or mean, μ, is the average contaminant concentration of the population. The dispersion or standard deviation, σ, is the square root of the variance of contamination for the population. The mean and standard deviation of the population are parameters. The deviation of the statistical mean from the population mean is the error associated with the analytical process. The standard deviation is associated with the uncertainty of the measurement that is affected by the analytical processes. Even if the population has a uniform (rectangular) distribution of the contaminant, the sampling distribution of sample means tends to be a normal (bell-shaped) distribution.

When a normal distribution is not assumed another approach to selecting the scalar k covering factor is to use the Chebyshev technique for selecting confidence levels and determining confidence intervals. Given a probability distribution with mean $X\text{-}bar$ and the standard deviation $s_{X\text{-}bar}$, the probability of obtaining a value within k standard deviations of the mean is at least $1 - 1/k^2$. Regardless of the assumption made about the distribution of the data, the probability of a measurement value from $X\text{-}bar - 3s_{X\text{-}bar}$ to $X\text{-}bar + 3s_{X\text{-}bar}$ is at least $1\text{-}1/3^2$ or 90% (k = 3). Chebyshev general theorem also applies to the special case of unimodal distributions. When the distribution is unimodal, the probability that X deviates from its mean by more than k times its standard deviation is less than or equal to $1/[2.25k^2]$. For a distribution with $X\text{-}bar$ is100 and s is 10, and where 3 is selected for k, the probability of any value, x, above 130 or below 70 is $1/[2.25(3)^2]$ or 4.0 %.

Assumption 2: Statistical Independence

The analytical subprocesses or components are statistically independent. This assumption is valid because the components are mutually exclusive. The process components are integral to the sample analysis process, but the uncertainty associated with each component is independent of the uncertainty of the other components. The uncertainty associated with sample preparation such as weighing with an analytical balance is independent of the uncertainty associated with instrumental analysis such as fluctuation in the power source.

The following example explains what is meant by statistical independence. A 1-gram subsample of a sieved, milled, and blended soil sample is weighed on an analytical balance. A 1-milliliter volume of traceable spike solution is added to the 1-gram of soil by using a Class-A glass pipette. There is an uncertainty associated with weighing the soil and there is an uncertainty associated with pipetting the spike solution, but these uncertainties are not dependent on each another. The uncertainty of the pipette does not affect the uncertainty of the balance.

The sequential analytical process uses different equipment, supplies, and techniques for the sampling and analysis procedures of each component. The uncertainties associated with the field sampling device used to collect the samples are independent of the uncertainties associated with gravimetric or volumetric measurements of the sample during preparation, and both are

independent of the uncertainties associated with instrument calibration such as energy spikes or reading fluctuation.

The estimated uncertainties are combined by a first-order Taylor series approximation of the measurement equation $y = f(x_1, x_2, \ldots x_n)$. The combined standard uncertainty of the measurement result y is $u_c(y)$, which is the square root of the estimated combined variance $u_c^2(y)$. The following equation is the Taylor series expansion for determining the estimated combined variance:

$$u_c^2(y) = \sum_{i=1}^{n} (\partial f/\partial x_i)^2 u^2(x_i) + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} (\partial f/\partial x_i)(\partial f/\partial x_j) u(x_i, x_j) \rightarrow 0$$

Equation 4.1

The second term in the equation accounts for the correlation or co-variance of variables. When two random variables are statistically independent their variances, s^2, are additive without the addition of the co-variance term. When two random variables are not statistically independent, the interdependence is taken into account through the introduction of their co-variance. For statistically independent variates, the co-variance is zero and the co-variant term drops out of the equation. The estimated co-variances or the estimated correlation coefficients are required if the variable x_i and x_j components are dependent. This simplifies the calculations to Equation 4.2**.** This equation is valid provided the variables are independent of each other.

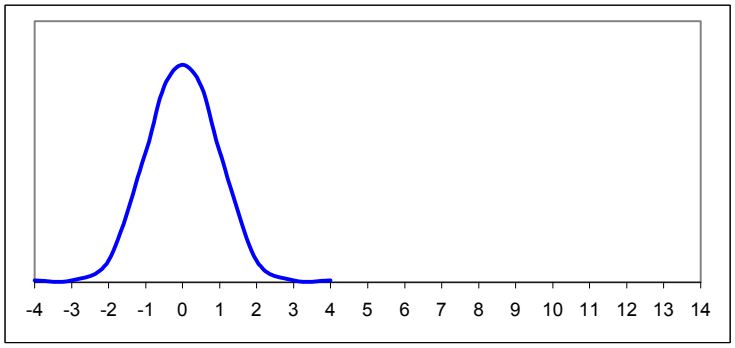
$$u_c^2(y) = \sum_{i=1}^{n} (\partial f/\partial x_i)^2 u^2(x_i)$$

Equation 4.2

Assumption 3: Proportional Uncertainty

The uncertainties are proportional and relative uncertainty is constant over the instrumental linear dynamic range (above the practical quantitation limit and below the limit of linearity or the instrument saturation limit). Analytical measurement is a combination of the background concentration and the sample analyte concentration. When an analytical instrument is standardized the instrument is zeroed at the background signal level. This electronic signal level is the noise. Since this zeroing of the instrument is subject to random variation the standard deviation of the electronic fluctuations is the standard uncertainty attributable to the background. This is demonstrated in Figure 4.1.

Figure 4.1



After standardizing the instrument, background measurements randomly fluctuate. However, the results are centered on zero with the measurements more likely near zero than far from zero. The uncertainty of the background is constant while the analyte concentration uncertainty is proportional to the analyte concentration. When the concentration of the analyte is low, the uncertainty of the background dominates. When the concentration of the analyte is high, the uncertainty from the analyte dominates. The following equation represents the combination of standard uncertainties from the background and analyte concentration:

Measurement = Background + Analyte Concentration

Equation 4.3

The uncertainty of the measurement ***(u_c)*** is calculated by taking the square root of the sum of the squares of the background standard deviation or standard uncertainty, u_{bkg}, and the analyte concentration standard deviation or standard uncertainty, u_{conc}^2**:**

$$u_c = (u_{bkg}^2 + u_{conc}^2)^{1/2}$$

Equation 4.4

Near the detection limit the background standard deviation is approximately equal to the analyte concentration standard deviation, and the equation for measurement combined standard uncertainty is calculated by the following equation:

$$u_c = (2u_{bkg}^2)^{1/2}$$

$$u_c = \sqrt{2}\,(u_{bkg})$$

Equation 4.5

When the measurement uncertainty is expanded to the 95% confidence from 30 or more measurement results the equation becomes:

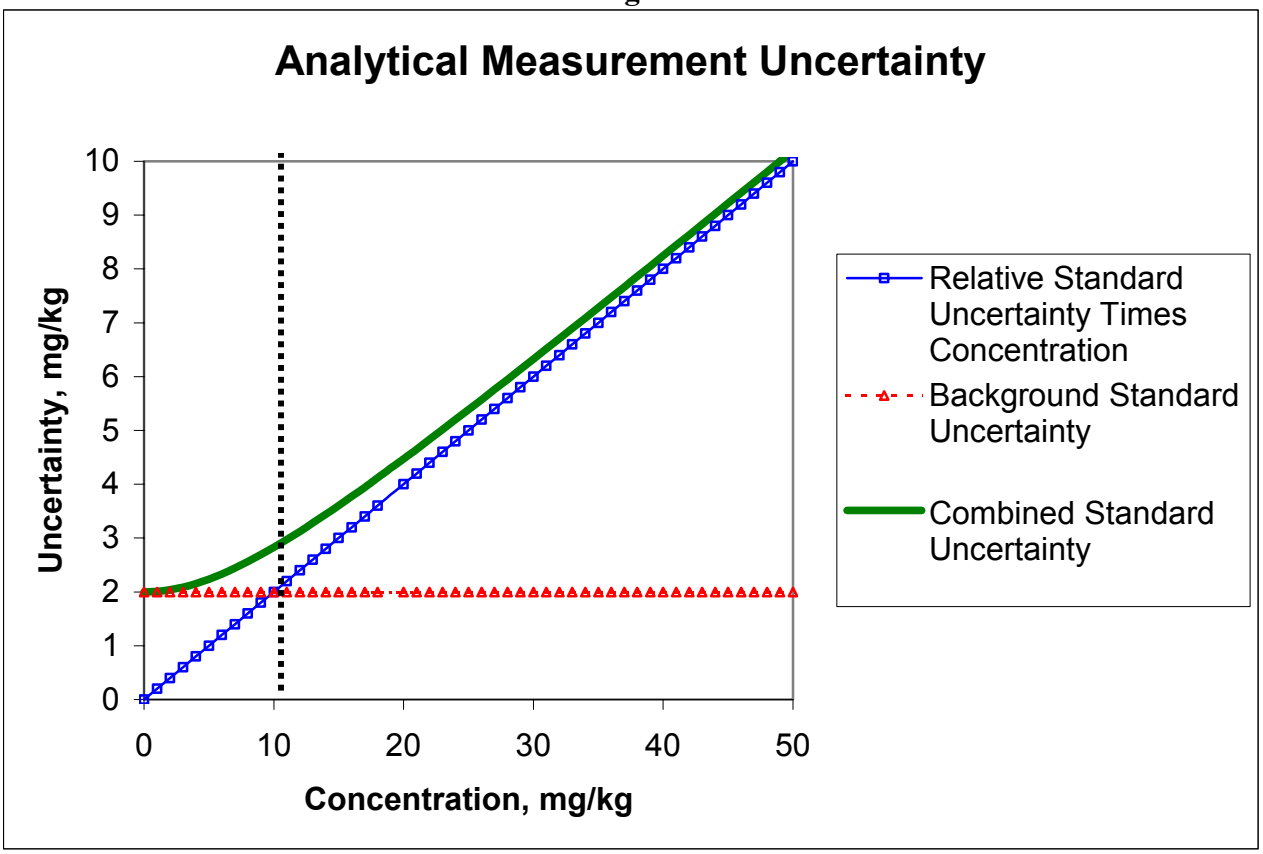
$$u_c = 2\sqrt{2}\,(u_{bkg})$$

Equation 4.6

Recovery efficiencies are reported in percent recovery and vary randomly on a scale proportional to analyte concentration with a constant relative standard deviation. For example, for trace metals analysis by ICP-AES, over the linear dynamic range, the uncertainty is approximately +/-10% of the concentration for the independent verification standard. At 10 ppm the uncertainty is 1 ppm while at 100 ppm the uncertainty is 10 ppm. Although the uncertainty increases proportionally to the analyte concentration beyond the practical quantitation limit (PQL) the relative uncertainty is constant as the analyte concentration increases until the instrument becomes saturated (above the linear dynamic range). With lower analyte concentration levels, the random variation in percent recovery is attributable to background "noise." As the analyte concentration level increases, the significance of background noise decreases. The uncertainty of the measurement becomes a function of the analyte concentration above the practical quantitation limit. If the standard deviation of the signal response increases proportionally with the analyte concentration, then the coefficient of variation is constant. At higher analyte concentration levels, the uncertainty becomes proportional to the analyte concentration and the relative uncertainty becomes a constant percent of the analyte concentration. The following graph represents the measurement uncertainty divided into two zones by a broken line. For the zone on the left, measurement uncertainty is dominated by

background noise. For the zone on the right, the measurement uncertainty is dominated by the analyte concentration.

Figure 4.2



The background uncertainty (u_{bkg}) is approximately 2 mg/kg at the 95% confidence level over the range of analyte concentrations. The analyte concentration relative standard deviation (s/C) (approximately 20% at the 95% confidence level) is multiplied with the analyte concentration (C). The product is the analyte concentration uncertainty for a particular level (u_{conc}). The uncertainties are combined by summing in quadrature.

Assumption 4: Multiplicative Relationship

The components are multiplicatively combined in the analytical system. This is demonstrated by analyte recoveries attributable to the components. Component uncertainty is a function of the recovery of the analyte, and analyte recovery is a multiplicative function that propagates through the analytical process. Recovery refers to the ability of the methodology to measure all of the analyte that is contained in the sample. The recovery of the analyte depends on the reliability of the processes of sample collection, preparation, and instrumental testing. Failure to recover the analyte is compounded by each component of the analytical system.

Analyzing the environmental contaminant concentration at a site requires collecting a representative sample, preparing a subsample of the collected sample, and testing the prepared sample by an analytical instrument. The measurement of reference materials or other samples of known composition are used to evaluate the recovery. In their absence, spikes or surrogates may

be added to the sample matrix. This is the most common method of determining analyte recovery for environmental samples. The sample preparation and testing processes are never completely efficient. Sample analyte recovery, R, is a function of the processes of sample collection, preparation, and measurement of the analyte concentration. The efficiency is the ratio of the measured concentration of the analyte, C_M, to the concentration reference value, C_T. For standards, spikes, surrogates, and tracers, the reference value is certified. Analyte recovery is determined by the following equation:

$$R = C_M / C_T$$

Equation 4.7

The sample recovery, R, of the analyte is a function of the combined sequential recoveries of the components.

Each component of the analytical process has an associated efficiency of recovering the analyte. This can be represented by the following equation:

$$R = \prod_{i=1}^{n} R_i$$

Equation 4.8

The term n is the number of components, R is the analyte recovery for the analytical process, and R_i is the analyte recovery for a particular component sub-process.

For multiplicative combination of standard uncertainties, the relative uncertainties are calculated. The relative standard uncertainty is represented by the standard deviation. For multiplicative functions such as $y = x_1 x_2$ where the uncertainties for sample preparation recovery, x_1 is $u_1(x_1)$, and for instrumental analysis recovery, x_2 is $u_2(x_2)$. The uncertainty (u_y) for y is calculated by the following equation:

$$(u_R / y)^2 = ((u_1(x_1)/x_1)^2 + ((u_2(x_2)/x_2)^2$$

Equation 4.9

In radiochemistry a carrier can be added to the sample and the preparation recovery can be calculated gravimetrically. Also, from radiochemistry a radioactive tracer can be added to the sample and the recovery of the tracer determined radiometrically. This is explained more fully in Appendix E. The components x_1 and x_2 affect the recovery efficiency of the analytical process represented by y. The standard deviations represent the absolute uncertainties, u_1 and u_2. However, because the function is multiplicative, the propagation of uncertainty is calculated by relative combined uncertainty. Relative uncertainty and absolute uncertainty are related by the following equation:

Relative Uncertainty = Absolute Uncertainty/Mean Value

Equation 4.10

The modeling of multiplicative combination of sample preparation and testing can be generalized to include all of the sampling and analysis components. The integrated system of components that make up the environmental analytical process can be modeled as a multiplicative combination and the percent recovery used to represent each component. Appendix B illustrates the hierarchical tiers of the nested approach. The analytical process can be broken down into field sampling activities and laboratory measurement activities. Co-located replicate samples can be modeled as the percent recovery of the average contaminant

concentration of the sample location area. The recovery of the contaminant analyte is a function of the heterogeneous distribution of the contaminant in the sampling location area. Field co-located replicates include the uncertainty associated with heterogeneity of the sampling location, the uncertainty associated with the sample collection and handling (preservation, storage, and transportation), and the laboratory activities. The field-split replicate samples can be modeled as the percent recovery of the average contaminant concentration of the collected sample from the sample location point. The recovery of the contaminant analyte is a function of the heterogeneous distribution of the contaminant in the collected sample. The field-split replicates include the uncertainty of the field activities of sample collection and handling, and laboratory activities.

The laboratory activities can be broken down into subsample preparation and test measurement. The subsample preparation can be modeled as the percent recovery of the contaminant analyte through drying, sieving, milling, blending, subsampling, extraction, digestion, distillation, separation, and precipitation processes. The recovery of the analyte during the subsample preparation is a function of the efficiency of the preparation process. The matrix effects on the analyte recovery affect the efficiency. A more robust preparation method would more efficiently recover the analyte than a less robust preparation method. The percent recovery of the analyte is a measure of the efficacy of the physical and chemical recovery process. The test measurement can be modeled as the percent recovery of the contaminant analyte during instrumental analysis. This includes matrix effects and the limitations of the instrumentation. Matrix effects that inhibit measurement of the analyte affect the instrumental analysis recovery.

Multiple sample locations are selected to represent the distribution of the contaminant of the sampling site population. Field samples are collected from the specified field sample locations. Adjacent to randomly selected field sample locations co-located samples are collected. Randomly selected field samples are homogenized and is split into field duplicate samples. In the laboratory, randomly selected field samples are sub-sampled for a matrix sample, matrix duplicate, and matrix spike samples. The laboratory duplicate sample represents the precision of the laboratory processes. The spike sample represents the accuracy of the laboratory processes. The duplicate sample must be spiked when the contaminant analyte level is less than the quantitation level.

Assumption 5: Combination of Component Uncertainty

The assumption that sample uncertainty is a combination of component uncertainty is valid because the analytical components are collectively exhaustive of the analytical process. By modeling the components of uncertainty to incorporate field sampling and laboratory analysis activities, the identified components completely describe all uncertainty sources. The analytical process is a multiple tiered hierarchy of discrete components that contribute to the analytical measurement uncertainty. Moving down the tiers of the "hierarchical chain" from the total study of the sampling site to the instrumental testing, analytical measurement uncertainty is compounded. Appendix B represents the tiered hierarchy for the analysis of total study uncertainty components. The sample analysis process is a sequential process that breaks down into discrete components, but each component is integral to the system. The relative combined uncertainty is determined by fractional sum in quadrature. Examples of the combination of components that contribute to analytical measurement uncertainty are provided in Appendix E.

Chapter 5: Summary

This guidance document presents a mechanism for estimating the environmental laboratory measurement uncertainty. The technical terms used in this document are defined in Appendix A. The mathematical model used in the study was published in the "Guide to the Expression of Uncertainty in Measurement" (GUM) by the International Organization of Standardization (ISO). Derivation of the mathematical model is explained in Appendix D.

With the nested approach, it is assumed that the components of the analytical process are collectively exhaustive and mutually exclusive for assessing measurement uncertainty. The quality control samples capture the uncertainties associated with routine sample collection, preparation, and testing. A nested approach combined with backward induction is required to determine the field sample analytical uncertainty. The uncertainty embodied in each sample result can be broken down into specific shells of uncertainty. This can be conceptualized as a hierarchical system of uncertainties "nested" within each other. The nested uncertainties are presented in Appendix C and the hierarchical relationships of the uncertainty components are presented in Appendix B.

The combination of the standard deviations of the intrinsic (instrumental) measurement effects (IME) and the preparation method effects (PME) represent the measurement uncertainty attributable to the laboratory activities. The measurement uncertainty attributable to the appropriateness of the analytical method is represented by the standard deviation of the matrix interference effects (MIE). This includes the physical preparation, subsampling, chemical preparation, and instrumental testing procedures. The sample collection uncertainty is attributable to the appropriateness sampling procedure equipment and technique for a specific analyte and media. This also includes the preservation and storage of the sample, and it is represented by the standard deviation of the sample collection effects (SCE). The sample location effects (SLE) represent the uncertainty associated with the appropriateness of the sampling strategy for capturing representativeness of the sampling plan by detecting local media contaminant distribution trends or "hot-spots." The sampling site media effects (SSE) represents the uncertainty associated with the contaminant distribution of the sampling site. After this information is acquired, the data user can develop more efficient and effective sampling and analysis strategies to improve data precision, accuracy, representativeness, completeness, and comparability. These revised strategies can be used to optimize the analytical process to balance the triple constraints of cost, time, and performance according to the data use.

The sampling site contaminant variability is found in the inherent large-scale and small-scale patterns of contamination. The pattern of contamination can vary spatially or temporally. The distribution of the contamination throughout the sampling site media must be captured to estimate the inherent contamination of the site. The analysis used depends on whether the samples collected for the environmental study are for a single discrete sampling event to determine spatial variation or a sequential sample collection schedule to determine temporal variation.

The pattern of contamination is broken down into large-scale patterns between sample locations for the sampling site and small-scale patterns within the sample location. Strategic sampling is used to capture this large-scale distribution of the contaminant at the delineated sampling site. Sampling strategies are designed to capture the site variation that includes the variation both in the matrix heterogeneity and in the concentration levels of contaminants throughout the site media. Representative sampling must accurately identify and define this

variation. Sample location distribution with relatively large distances between sampling points or a biased sampling approach fails to identify the contaminant site variation. When sampling site contaminant levels vary significantly, representative-sampling strategies must include more samples and a stratified approach to sampling to reduce uncertainty.

The small-scale (within the sample location representative area) variation can be estimated by incorporating co-located samples into the sample plan. The strategic use of co-located samples captures localized contaminant variation and quantifies the efficacy of the sampling strategy. Same site samples collected from neighboring locations and samples collected at different times, but from the same sample location, can be analyzed to determine inter-sample spatial and temporal variation. Sampling methodologies are designed to incorporate appropriate sampling equipment and procedures that prevent incomplete recovery of the contaminant and cross-contamination from inadequate equipment decontamination. The environmental laboratory prepares and tests routine environmental samples and the efficacy of the laboratory measurement process is assessed by matrix spike samples, laboratory control samples, and calibration verification standards.

The variations in the technique and equipment used during sample collection affect the analytical process. The sample collection component of the analytical process includes the sample collection, field homogenization, preservation, transportation, and storage. A field-split duplicate captures the variability of the sample collection process when the field and field-split are sent to the same laboratory for analysis as separate samples.

Generally, subsampling, extraction and instrumental effects are the largest sources of laboratory systematic error. Subsampling is a significant source of uncertainty when relatively small subsamples are prepared and tested, or because of the heterogeneity of the sample contaminant distribution. The variation in the method used during sample preparation affects the analytical process and compounds analytical variability. The sample preparation component of the analytical process includes the subsample reduction, physical preparation such as drying, milling, and blending, and chemical preparation such as extraction, concentration, and separation procedures. Sample matrix interferences affect the recovery of the analyte during sample preparation and instrumental analysis. Matrix interference is identified and determined by matrix interference samples such as matrix spike, matrix duplicate, surrogate, and tracer samples.

Variations in the instrumental analysis affect the analytical error and uncertainty. The intrinsic measurement variability is attributable to several factors including: random electronic fluctuation, systematic instrumental drift, degradation of the signal from equipment failure and environmental fluctuation, operator error such as blunders or bias, and sample geometry and matrix effects. The instrumental variability is identified and determined by the matrix interference samples, the laboratory control sample, the initial calibration standard, the independent calibration verification standard, and the continuing calibration verification standard.

Once the component uncertainties have been estimated, the single test measurement uncertainty, uncertainty attributable to laboratory measurement activities, and uncertainty attributed to field sampling activities can be estimated by integrating the appropriate components. For example, the data user can identify the sources of uncertainty with particular laboratory or field activity and determine the appropriateness of a certain method. Examples of the nested approach are presented in Appendix E.

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Appendix A: Glossary

Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random variation (precision) and systematic error (bias) components that are attributable to sampling and measurement operations.

Action level: The contaminant concentration used by the environmental decision-maker to determine whether an environmental site or population is in compliance with regulatory threshold standards or risk-based concentration levels.

Analyte: An analyte is the element, compound, or species that is identified or determined through analysis.

Analytical process: The combined sampling and analysis process that includes sampling design, and sample collection, preparation, and testing.

Analytical measurement uncertainty: Combined standard uncertainty that is derived from the multi-tiered analytical process.

Analytical measurement uncertainty propagation: Examination of how uncertainty in individual components of the analytical process affects the analytical measurement uncertainty.

Backward induction: Process of estimating the particular component standard uncertainties from the general measurement combined standard uncertainty. The process is counter current to the cause-and-effect graphical presentation where particular component standard uncertainties are estimated and inductively combined to produce a generalized measurement combined standard uncertainty. With the nested approach, unknown component standard uncertainties are "backed-out" of the known measurement combined standard uncertainty by the nested hierarchical approach.

Batch: Environmental samples that are prepared and measured together with the same process and personnel, using the same lot(s) of reagents. Samples are combined in batch because they have similar matrices and they behave similarly under the same preparation and testing procedures.

Bias: The bias of a measurement is all error that cannot be attributed to random variation. Bias is the systematic error inherent in a method such as extraction inefficiencies or caused by some artifact of the measurement system such as double spiking.

Blank: A blank is a quality control sample used to detect and identify contaminants introduced to samples during the measurement process.

Blunders: Blunders are human errors that produce outlying results and that are detectable as exceptional measurements by statistical analysis, but they cannot be treated by statistics. Analyst errors are the result of carelessness, lack of knowledge or experience, and personal bias. Contamination during the preparation process and accidentally adding double the prescribed amount of spiking solution (double-spike) are examples of blunders.

Boundaries: The site or population spatial (area) and temporal (time period) conditions and constraints the data are collected and decisions are applied. Samples are collected within the site boundary.

Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter, instrument, or other measuring devise.

Cause-and-effect diagram: A graphical representation of the component uncertainty effects that cause measurement uncertainty. The particular component effects are inductively combined to cause the measurement effect uncertainty. A popular diagram is the Ishikawa fish-bone diagram.

Co-located replicate samples (CLR): Co-located replicate field sample is a second sample collected at the same location area as the original sample. The CLR is collected 0.5 to 3.0 feet from the original sample using the same recovery techniques, but treated as a separate sample. The sampling interval between routine field samples should be at least 3 times greater than the distance of the co-located sample from the original field sample. For example if the adjacent field sample is 10 feet from the original field sample, then the co-located sample should be 3 feet from the field sample. CLR is used to assess the local area variability of contamination at the sampling location and it is used to evaluate the efficacy of the sampling strategy.

Combined standard uncertainty: The standard uncertainty of a measurement result derived from the combination of component standard uncertainties.

Control chart: A control chart is a tool for using statistically derived control limits as the basis for real-time data quality analysis and long-term trend analysis.

Control limits: Control limits may be specified in a reference Method (either as mandatory or guidance limits), or may be developed by a laboratory using internal performance data. Control limits represent acceptance criteria for determining whether an analytical system is in control.

Data reduction: The process of transforming raw data by arithmetic or statistical calculations, calibration standard curves, or concentration factors, and collation into a more useable and informative form.

Duplicates or replicates: A duplicate or replicate sample is a quality control sample, which is used to determine the precision associated with all or part of the sample collection and measurement process.

- Field duplicates are used to determine the precision associated with the entire sample collection and measurement process. Field duplicates are two independent samples that are collected either as nearly as possible from the same point in space and time (field-split) or from 0.5 to 3.0 feet from the original sample (co-located), but within the sample collection area. The two field duplicate samples are collected from the same source, using the same type of sampling equipment. Each field duplicate is collected and stored in separate sample containers and transported in the same shipping container.
- Laboratory duplicates include matrix duplicates and matrix spike duplicates. A matrix duplicate (usually called a laboratory duplicate) is used to determine the precision of the intra-laboratory analytical process for a specific sample matrix. A laboratory sample and its associated matrix duplicate are prepared in the laboratory as subsamples, carried through the entire measurement process as independent samples. A matrix spike sample and its associated matrix spike duplicate are prepared in the laboratory as subsamples, and each is spiked with identical, known concentrations of target analyte(s).

Equipment blanks (rinseate blanks): Quality control samples of analyte-free media that have been used to rinse the sampling equipment after use. They are collected after the equipment decontamination and prior to resampling.

Error: Error is the systematic difference of the measurement result from the actual measured value The precision can be calculated from multiple measurements as the standard deviation or from two measurements as the relative percent difference. Errors are additive if the value is constant regardless of the concentration of constituents. Additive errors include solubility of a precipitate and incorrect blank correction (subtraction). Proportional errors change according to the amount of the concentration of contaminant analyte or analytical interferent.

Expanded uncertainty: The estimated uncertainty interval bracketing the result of a measurement that is expected to incorporate a certain fraction of the distribution of values

reasonably attributed to the measurement value. The combined standard uncertainty is multiplied by a coverage factor that represents the confidence level.

Field blanks: A quality control sample that is transferred from one vessel to another, or exposed to the sampling environment at the sampling site. They are used to measure incidental or accidental sample contamination during sampling and analysis.

Field-split replicate samples (FRS): Field-split duplicate samples are collected from one location point, divided into separate containers, and handled as separate sample throughout the sample process. They assess sample heterogeneity, sample methods, laboratory preparation methods, and laboratory instrumental analysis methods.

Instrument calibration standards (ICS): Traceable standards used to standardize the instrument and establish the correlation between analyte concentration and instrumental signal response.

- External standards are measured amounts of the analytes added to analyte-free sample geometry suitable for instrumental analysis with a known final concentration. For example, the external standard for ICP is acidified water with traceable concentrations of analytes. Another example is a stainless steel planchette with traceable concentration of analytes for gross alpha and gross beta radioactive counting.
- Internal standards are measured amounts of certain compounds added to all samples after preparation or extraction of the sample, but before instrumental analysis. Internal standard correction is used to assess the analytes of interest recoveries that are affected by column injection losses, purging losses, and viscosity effects. Analytes of interest recovery are normalized to the internal standard recovery.

Intrinsic instrumental measurement uncertainty: The uncertainty associated with instrumental analysis repeatability that is the variability of data generated when the same sample is determined using the same testing instrument.

Intrinsic instrumental measurement effects (IME): Variations in the repeatability of the analytical measurement system are the IMEs.

Laboratory control sample (LCS): A quality control sample that consists of a known spike with a known amount of targeted analytes. Laboratory control sample is analyte-free water for aqueous analyses or Ottawa sand for soil analyses spiked with known concentrations of analytes of interest and carried through the complete sample preparation and analysis procedure. LCSs are used to verify the laboratory performance of the method in a clean matrix without interferences.

Limiting mean: The value approached by the average of sample measurement as the number of measurements made by a stable measurement process increases indefinitely. The limiting mean may be biased or unbiased compared to the population mean.

Linearity limit: The upper limit of concentration or amount of substance that incremental additions of analyte produce constant increments of response.

Matrix: The sample matrix is the component or substrate that contains the analyte(s) of interest that is collected from the sampling site media. Samples with similar matrix have the similar interferences and affect the performance of the preparation and testing procedures similarly. Matrix quality control samples are used to assess the affect of the sample matrix on recovery of the analyte(s) of interest.

- **Aqueous**: Any aqueous sample including surface water, groundwater effluent water, and toxic characteristic leaching procedure (TCLP) or other aqueous extracts, but not drinking water.

- **Drinking water**: Any aqueous sample that has been designed a potable or potentially potable water source.
- **Saline/estuarine**: Any aqueous sample from an ocean or estuary, or other salt-water source such as the Great Salt Lake.
- **Non-aqueous liquid**: Any organic liquid with less than 15 percent settleable solids.
- **Biological tissue**: Any sample of a biological origin such as fish tissue, shellfish, or plant material.
- **Solids:** Includes soil, sediment, sludge, and other matrices with greater than 15 percent settleable solids.
- **Chemical waste**: A product or by-product of an industrial process that results in a matrix not previously defined.
- **Air:** Whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas or vapor that are collected with a sorbant tube, impinger solution, filter or other devise.

Matrix interference effects (MIEs): Variations in extraction, concentration, and separation recoveries during sample preparation caused by the matrix that affects analyte recovery. Interferents overlap or mask the regions of interest for analytes of interest peaks are MIEs. These include ICP-AES spectral wavelength, ICP-MS and GC-MS charge to mass ratio spectrum, GC elution of compounds retention time windows, and radioanalytical ionization energies. A separate subsample of the sample can be spiked or a standard can be added to the sample before preparation and instrumental testing.

Matrix interference sample (MIS): Matrix samples are used to assess the matrix interferences on the preparation and instrumental testing processes. The matrices include: aqueous such as surface water and groundwater, potable drinking water, saline water such as seawater, salt-lake water, and estuary water, non-aqueous liquids, biological tissue, concrete, sediment, industrial sludge, high clay content soil, and sandy soil. To the matrix sample is added a known amount of spike, surrogate, tracer, or carrier to determine matrix interference on the recovery of the analyte.

- Matrix spikes and matrix spike duplicates are subsamples of environmental sample spiked with known concentrations of analytes of interest, and carried through the sample preparation and instrumental analysis procedures. Matrix spikes are used to assess the analyte recovery for the sample matrix. The use of matrix spikes is recommended for organic methods, inorganic methods such as ion chromatography, wet chemistry, trace metals analyses, and radioanalytical methods.
- Surrogates are organic compounds that are similar to the analytes of interest in chemical composition and behavior in the analytical process, but are not normally found in environmental samples, and surrogates do not interfere with the analytes of interest. Surrogates of known concentration are added to all samples and carried through the complete sample preparation and analysis procedure. Surrogates are used to assess the organic analyte recovery for the sample matrix.
- Tracer is a radioisotope of the radionuclide of interest, but with a different atomic mass. Tracer of known radioactivity is added to all samples before the sample preparation and analysis procedure. The tracer is used to assess the analyte recovery for the sample matrix. Analytes of interest radioactivity recovery are normalized to the tracer recovery.
- Carrier is a non-radioactive isotope of the radionuclide of interest. Carrier of known concentration is added to all samples before the preparation and analysis procedure. The

Carrier is used to assess the analyte recovery for the sample matrix. Sample results are gravimetrically normalized to the carrier recovery.

- Interferent check sample includes both the low concentration analytes of interest alone (ICSA), and the low concentration analytes of interests along with high concentration interfering elements (ICSAB) used in inductively coupled plasma (ICP). The ICS is used to assess the background and inter-element correction factors.

Matrix spike (MS): A matrix spike is an subsample of sample that is spiked with a known concentration of target analyte(s) prior to sample preparation. The MS/MSD results measure the performance of the method relative to the sample matrix. Analyte recoveries for MS samples verify the laboratory performance of the method for a specific matrix with interferences.

Matrix spike duplicate (MSD): A matrix spike duplicate is used to determine the precision of the intra-laboratory analytical process for a specific sample matrix. A matrix spike sample and its associated matrix spike duplicate are prepared in the laboratory as split samples, and each is spiked with identical, known concentrations of target analyte(s).

Mean: The central tendency of the population, μ, or sample, η. The average of a set of data is an estimation of the sample and population means. The data mean, ***X-bar***, is the sum of the analyte measurement results divided by the number of measurements. The sample mean is the average analyte concentration value in a sample that is estimated by the sample data mean. The population mean is the average analyte concentration for the population value that is estimated by sampling site data mean.

Measurement uncertainty: The range of measurement results that the measurement mean is estimated to be located. Measurement uncertainty is affected by many components that compound the dispersion of results that are attributed to the measured value. Uncertainty is the random variation of the measurement result from the actual measured value. The components of measurement uncertainty are identified as measurement variation or precision (random or stochastic variations) and uncertainty associated with the estimation of the measurement bias (determinate or systematic error).

Method: A published sample preparation and analysis procedure. Regulatory agencies or associates, including EPA, ASTM, AIHA, and state agencies publish reference methods for environmental analysis.

Matrix specific: Matrix specific refers to an attribute that is associated with a specific sample matrix. Matrix specific quality control or proficiency testing samples are used to evaluate the affect of sample matrix on method performance.

Nested hierarchical approach: Measurement uncertainty estimation method used to estimate component uncertainties of the environmental field sample single test measurement by deriving component uncertainties from quality control samples and standards. Environmental samples and standards are conceptualized as nested hierarchies of components that affect the uncertainty of the measurement result. The process of backward induction is used to estimate the uncertainty of each nested tier of the analytical process hierarchy. Backward induction starts with the simplest tier and works to the most complex tier. At each tier of the hierarchy, the "known" estimated uncertainties of components and samples or standards are used to estimate the "unknown" component uncertainty.

Normalization: Mathematical procedure where systematic error of the measurement is corrected by dividing the test measurement result by the percent recovery of the reference value.

Parameter: The population average contamination concentration and the range of contamination concentrations of the environmental population. The average concentration parameter

characterized by the mean (symbolized by μ) and the range of contamination is characterized by the standard deviation (symbolized by σ).

Partitioning: The analytical process of breaking down the total study uncertainty into component sources of uncertainty that includes the inherent population variability and the measurement uncertainty. The measurement uncertainty is partitioned into sampling design, sample collection, sample preparation, and sample testing uncertainties.

Precision: The degree of mutual agreement characteristic of independent test measurements as the result of repeated application of the process under specified conditions.

Preparation method effects (PMEs): Variations in gravimetric and volumetric measurements of the sample preparation process and deviations in the analytical method preparation procedure that affect recovery of the analyte are PMEs. These include variation in pH that affects solubility of the analyte and normality of the reagents that affect efficacy of the extraction, separation, and concentration of the analytes of interest.

Population: A generic term denoting any finite or infinite collection of individual things, objects, or events. The environmental site is the population that is sampled to estimate the contaminant parameters.

Probability: The likelihood of the occurrence of any particular event, estimated as the ratio of the number of times that the event occurred and the number of possible occurrences of the event.

Quality assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

Quality control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

Quality system: A structured and documented management system describing the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products, and services.

Quantitation limit: The minimum level, concentration or quantity of a target analyte that can be quantified with the confidence level required by the data user. By convention, the quantitation limit is 10 times the standard deviation of the lowest level of measurement. The uncertainty associated with this limit can be ± 30% at the 95% confidence level.

Random Variation: The variability inherent in any analytical process that varies in sign and magnitude, but the average of random variation approaches zero when enough measurements are made.

Replicate: A repeated sample or test measurement. A replicate is the general case while a duplicate is the special case consisting of two samples or measurements.

Replicate analyses: The measurements of the variable of interest performed identically on two or more sub-samples of the same sample within a short time interval.

Sample: A representative portion of the environmental site population that is collected to characterize the composition of the population contaminant parameters.

Sample collection effects (SCEs): Variations in the collection process, sample containers, preservation, storage, and hold times of the samples are SCEs. These include improper decontamination of the collection equipment and improper acidification of aqueous metals samples, and improperly cooling the soil samples. Also included in the SCEs is the sampling devise collection efficiency or the collector efficiency for the recovery of the analyte of interest.

Sample location effects (**SLE):** Variations in the contamination concentration of the area of the sample location are SLEs. Standard uncertainty (standard deviation) estimation is required to determine the efficacy of the sampling design to capture the local variations in the contamination distribution of the site, and identifying "hot-spots," or localized contamination such as radioactive particles and small-scale spills.
Sampling: The process of collecting representative samples that includes location of the sample within the population boundaries and the collection of a subset of the population.
Sampling design: The strategic number of samples, and location or timing for collection of samples based on systematic, and random approaches to capture stratified, "hot-spots," or average contamination of the environmental site. Sample collection includes single increment "grab" samples or "composite" combination of single increment samples.
Sampling event: A sampling event is a sequential implementation of a strategic sampling plan at a single contiguous site for a single matrix. A sampling event begins with collection of the first sample. A sampling event ends when sampling at the site is discontinued for an extended period, if the ambient conditions at the site change, or if an unanticipated change in the sample matrix is encountered.
Sampling frame: List that identifies all of the population sampling locations from which samples can be selected.
Sampling site effects (SSEs): Variations in the environmental site contamination distribution are SSEs. The sampling site effects are the inherent or natural variability that the environmental study plans to capture. Sampling plans are designed for determining sampling frequencies such as per day timing or intervals such as 10-foot grid spacing. The strategic location and frequency of samples is planned to characterize contaminant distribution patterns, estimate average concentration of contaminants, detect "hot-spots", and map trends such as large-scale migration over time.
Sampling site field samples (SFS): Sampling site field samples are samples collected from the sampling site media to represent the population contaminant distribution. The number, timing, and location of sampling site field samples are planned before sample collection according to the sampling strategy.
Sampling units: The sampling locations from which samples are collected.
Selectivity: The capability of an analytical chemistry test method to respond to a target substance or constituent in the presence of non-target substances or interferents.
Sensitivity: The capability of a method or instrument to discriminate between measurement response representing different concentration levels of a variable of interest.
Split sample: A field duplicate split sample is used to assess intra- or inter-laboratory precision of the measurement process. Field-split samples are obtained by preparing two or more individual subsamples after thorough homogenization, in the field, of a single sample. A field-split sample is used to determine intra-laboratory precision if the split samples are submitted to a single laboratory. A field-split sample is used to determine inter-laboratory precision if the split samples are submitted to different laboratories.
Spike preparation effects (SPEs): Variations in the pipetting, dilution, and transfer of traceable standard solutions for making quality control samples are SPEs. Traceability includes lot and serial tracking to a reference standard as well as concentration or activity, uncertainty interval, confidence level, and serial dilution information.
Standard deviation: Measure of the spread or dispersion equal to the square root of the variance. The following equation is used to calculate the standard deviation:

$$s^2 = (\sum_{i=1}^{n}(x_i - X\text{-}bar)^2)/(n-1)$$

$$s = ((\sum_{i=1}^{n}(x_i - X\text{-}bar)^2)/(n-1))^{1/2}$$

The term ***s*** is the standard deviation. The standard deviation squared, s^2, is the variance. The term $\sum(x_i - X\text{-}bar)^2$ is the mean, ***X-bar,*** of the measurements subtracted from individual measurements, x_i . The difference between each individual measurement and the means is squared and then summed. The term ***n*** is the number of measurements. The term ***(n – 1)*** is used to determine the degrees of freedom associated with the equation. This is the variance of the measurement. The square root of the variance is taken to calculate the standard deviation. The population parameter standard deviation, σ, is estimated from the sample statistic standard deviation, ***s***, that is calculated from measurement results. The standard deviation represents the standard uncertainty.

Standard uncertainty: The standard deviation of replicate measurements or an estimated standard deviation represents the standard uncertainty of each component of measurement uncertainty.

Surrogate: A surrogate analyte is used to monitor method performance on a matrix-specific basis. A surrogate is a pure analyte that is added to the subsample in known amount, prior to sample extraction. The surrogate, is similar to the method target analytes in composition and behavior, but is not ordinarily found in environmental samples. Because surrogates are generally added to each sample in a batch, they can be used to monitor recovery on a sample-specific, rather than batch-specific basis.

Target analyte: A target analyte is the element, compound, or class of compounds that is detected and quantified through the analytical measurement process.

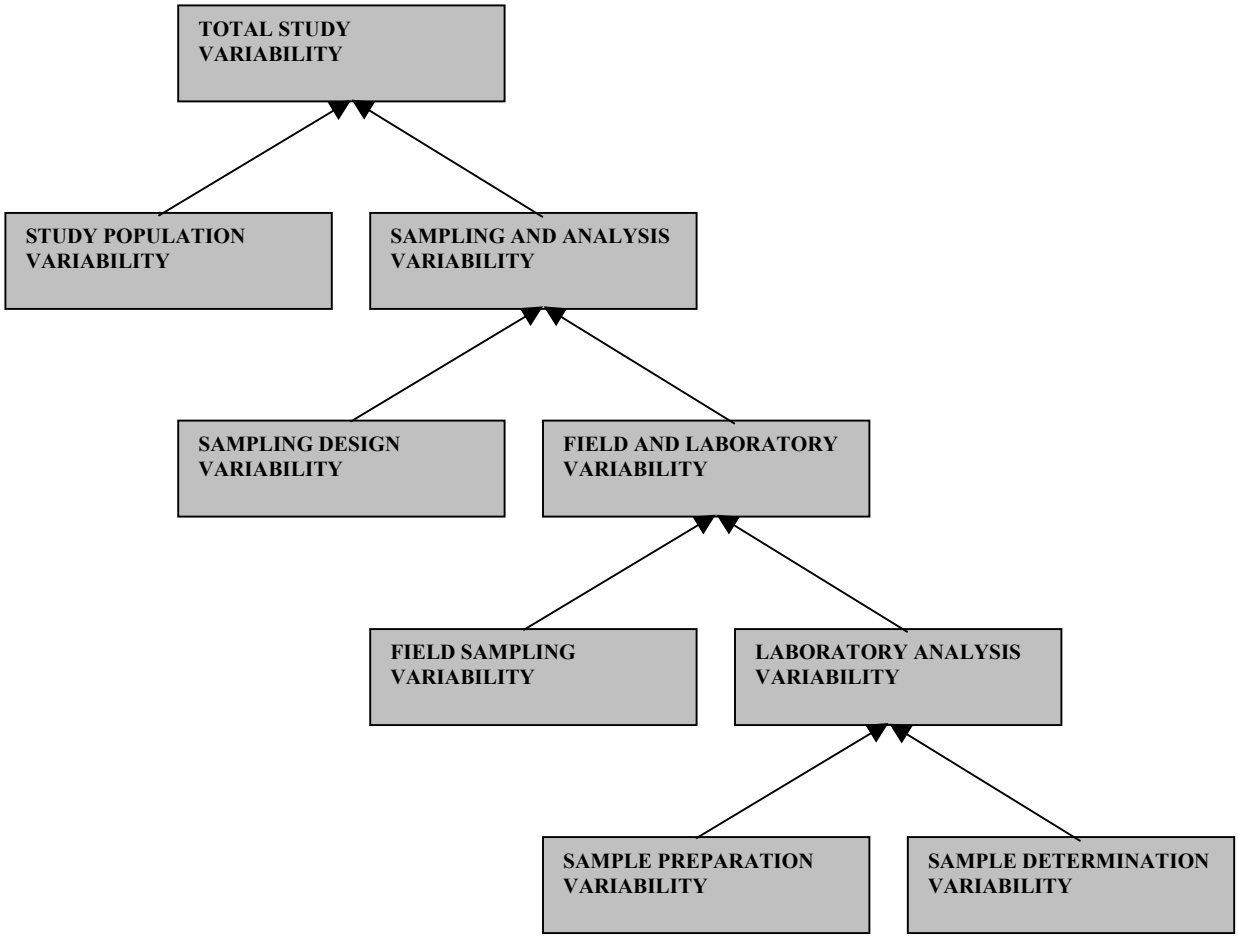
Test: A technical operation that consists of the identification or determination of an analyte of a prepared sample according to a specified procedure. The analytical result of a test is the test measurement.

Traceability: The property of a result of a measurement whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons. The ability to trace the source of uncertainty of a measurement or a measured value.

Trip blanks (transport blanks): Quality control samples that are analyte-free media taken from the laboratory to the sampling site and returned to the laboratory unopened. They are used to measure cross-contamination from the container and the preservative during the sampling process.

Appendix B:

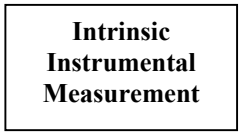
FIGURE B: HEIRARCHY OF TOTAL STUDY VARIABILITY COMPONENTS



Appendix C: The Nested Hierarchy Model

The following figures represent the uncertainty components of analytical samples, and the equations represent the mathematical model used for analyzing the nested uncertainties.

Figure C.1: Instrument Calibration Standard

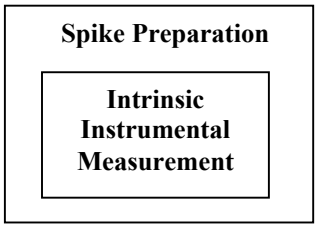


The instrument calibration standard is used to standardize the test instrument. The calibration independent variable is the analyte concentration and the dependent variable is the instrument response. Once the instrument is calibrated, the standard is reanalyzed and reported in concentration units. The relative standard deviation of the instrument calibration standard (ICS) reanalysis is equivalent to the uncertainty associated with the intrinsic (instrumental) measurement variation (IME). The IME is the analytical repeatability. By estimating the intrinsic measurement uncertainty the precision of different analytical instruments can be compared.

$$^{ICS}u_r = {}^{IME}u_r$$

Equation C.1

Figure C.2: Independent Calibration Verification Standard



The independent calibration verification (ICV) standard is a second source standard analyzed to verify the standardization of the test instrument. The ICV incorporates:

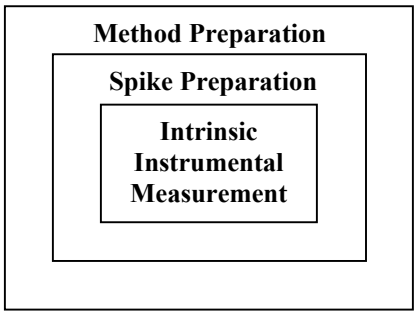
- intrinsic instrumental measurement repeatability,
- uncertainty associated with the second source standard, and
- uncertainty associated with preparation of the standard.

The relative standard deviation of the independent calibration verification (ICV) is equivalent to the uncertainty associated with the IME combined with the spike preparation uncertainty (SPE).

$$(^{ICV}u_r)^2 = (^{IME}u_r)^2 + (^{SPE}u_r)^2$$

Equation C.2

Figure C.3: Laboratory Control Sample



The laboratory control sample (LCS) is an analyte-free and interferent-free, clean matrix sample (such as deionized water) spiked with a second source standard and processed through the preparation and instrumental analysis processes. The LCS incorporates:

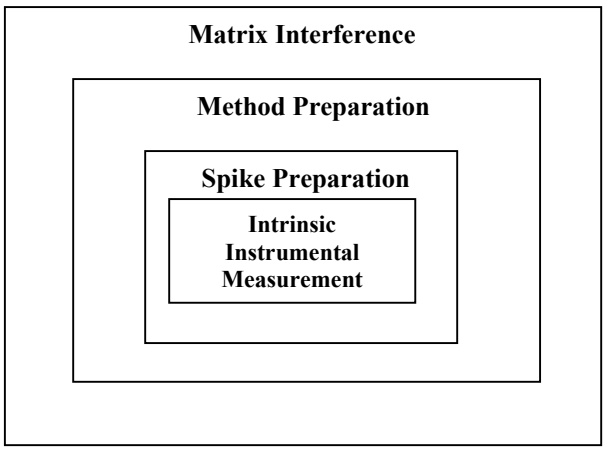
- intrinsic instrumental measurement repeatability,
- uncertainty associated with the second source standard,
- uncertainty associated with preparation of the standard, and
- uncertainty associated with the analytical method preparation procedure.

The relative standard deviation of the laboratory control sample (LCS) is equivalent to the uncertainty associated with the IME combined with the SPE and the method preparation effects (PME). By estimating the uncertainty of the analytical preparation procedure, the precision of different preparation methods in a clean matrix can be compared.

$$({}^{LCS}u_r)^2 = ({}^{IME}u_r)^2 + ({}^{SPE}u_r)^2 + ({}^{PME}u_r)^2$$

Equation C.3

Figure C.4: Matrix Interference Sample



The matrix interference sample is a routine field matrix sample spiked with a second source standard and processed through the preparation and instrumental analysis processes. The matrix interference sample incorporates:

- intrinsic instrumental measurement repeatability,
- uncertainty associated with the second source standard,
- uncertainty associated with preparation of the standard,
- uncertainty associated with the analytical method preparation procedure, and

- uncertainty associated with the matrix interference.

The relative standard deviation of the matrix sample (MIS) is equivalent to the uncertainty associated with the IME combined with the SPE, PME, and matrix interference effects (MIE). By estimating the uncertainty of the matrix interference, the precision of different preparation and testing method combinations in "real-world" samples can be compared.

$$({}^{MIS}u_r)^2 = ({}^{IME}u_r)^2 + ({}^{SPE}u_r)^2 + ({}^{PME}u_r)^2 + ({}^{MIE}u_r)^2$$

Equation C.4

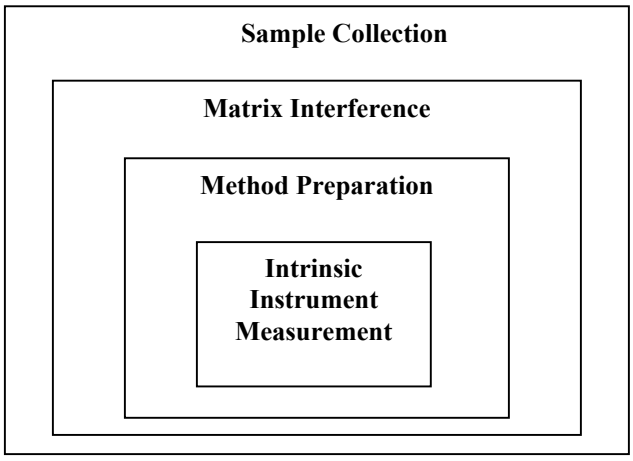


Figure C.5: Field-Split Replicate Sample

The field-split replicate sample is a field sample that is split into two subsamples in the field, but treated as two separate samples. The field-split replicate is prepared and analyzed with the other field samples. The field-split replicate incorporates:

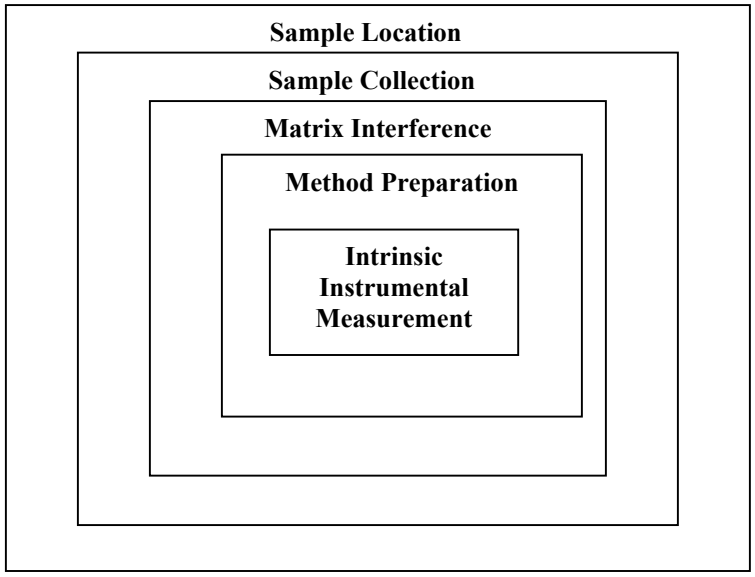
- intrinsic instrumental measurement repeatability,
- uncertainty associated with the analytical method preparation procedure,
- uncertainty associated with the matrix interference, and
- uncertainty associated with the sample collection process.

The relative standard deviation of the field replicate split (FSR) sample is equivalent to the uncertainty associated with the IME combined with the PME, MIE, and the sample collection effects (SCE). By estimating the uncertainty of sample collection process, the precision of sample collection at the sample location point can be evaluated.

$$({}^{FSR}u_r)^2 = ({}^{IME}u_r)^2 + ({}^{SCE}u_r)^2 + ({}^{MPE}u_r)^2 + ({}^{MIE}u_r)^2$$

Equation C.5

Figure C.6: Co-Located Field Sample



The co-located replicate sample is a field sample that is located from 0.5 to 3.0 feet away from the original field sample, but treated as two separate samples. The co-located replicate sample is used to assess sample location area variation and the efficacy of the sampling strategy. The co-located replicate is prepared and analyzed with the other field samples. The co-located replicate incorporates:

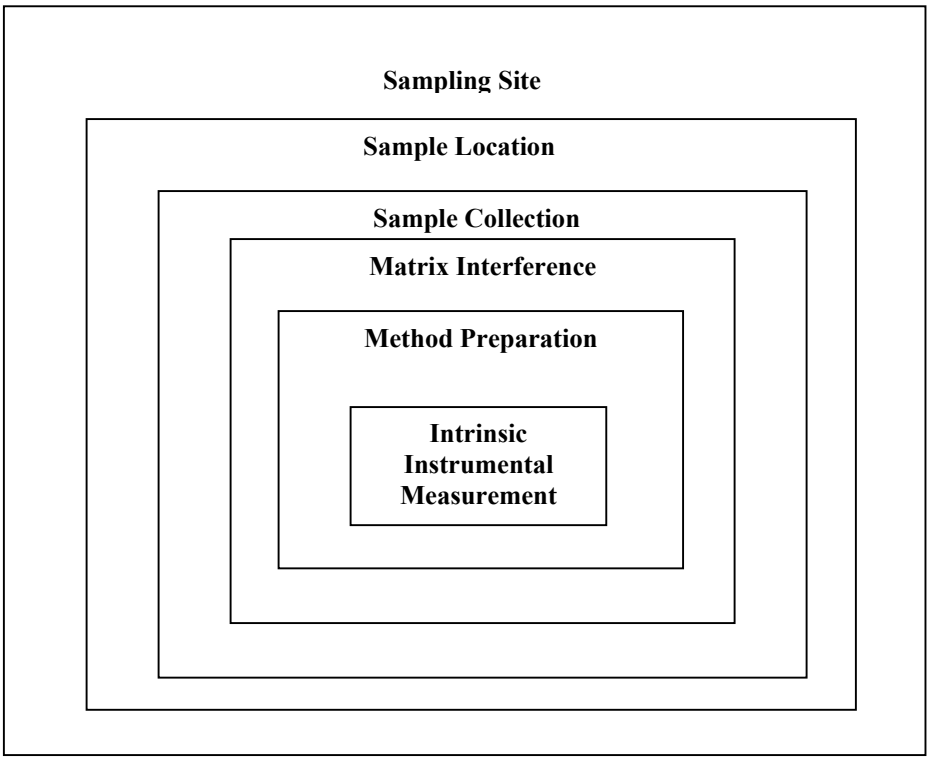
- intrinsic instrumental measurement repeatability,
- uncertainty associated with the analytical method preparation procedure,
- uncertainty associated with the matrix interference,
- uncertainty associated with the sample collection process, and
- uncertainty associated with the local variability of the contamination around the sample location and between sample locations.

The relative standard deviation of the co-located replicate (CLR) sample is equivalent to the uncertainty associated with the IME combined with the PME, MIE, SCE, and the sample location area effects (SLE). By estimating the uncertainty of co-located samples, the precision of sampling strategy for the sample location area can be evaluated.

$$({}^{CLR}u_r)^2 = ({}^{IME}u_r)^2 + ({}^{SCE}u_r)^2 + ({}^{PME}u_r)^2 + ({}^{MIE}u_r)^2 + ({}^{SLE}u_r)^2$$

Equation C.6

Figure C.7: Site Field Samples



The routine field samples are used to study the environmental sampling site. The total study uncertainty is the collective variability that incorporates:

- intrinsic instrumental measurement repeatability,
- uncertainty associated with the analytical method preparation procedure,
- uncertainty associated with the matrix interference,
- uncertainty associated with the sample collection process,
- uncertainty associated with the variability of contamination around the sample location and between sample locations, and
- inherent population variability of contaminant distribution in the sampling site media.

The relative standard deviation of the collection of site field samples (SFS) is equivalent to the uncertainty associated with the IME combined with the PME, MIE, SCE, SLE, and the sampling site effects (SSE). By estimating the uncertainty of routine field samples, the precision of inherent or natural variability of the sampling site population can be evaluated.

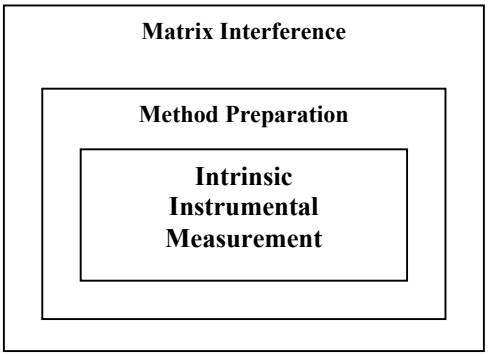
$$({}^{SFS}u_r)^2 = ({}^{IME}u_r)^2 + ({}^{SCE}u_r)^2 + ({}^{PME}u_r)^2 + ({}^{MIE}u_r)^2 + ({}^{SLE}u_r)^2 + ({}^{SSE}u_r)^2$$

Equation C.7

Using the nested hierarchical approach, the component uncertainties are "backed-out" of the quality control sample standard deviation. The standard deviation is "backed-out" of the statistical quality control limits. The component uncertainties for routine analytical samples are integrated to determine their relative uncertainty. In addition, the systematic error estimate can be "backed-out" of the percent recovery of the reference value and used to normalize the

integrated uncertainty for routine samples. The following nested hierarchy represents the uncertainties routinely associated with laboratory activities for field samples.

Figure C.8: Field Sample: Laboratory Activities



Notice that there are three sources or components of uncertainty associated with the laboratory activities that are incorporated into the routine field samples. Once these component uncertainties have been "backed-out" of the quality control sample uncertainties, the laboratory can estimate the effect of their activities on the sample measurement uncertainty from these components. Matrix interference uncertainty estimation is the best approximation of the matrix effects, but it is not exact. However, the uncertainty associated only with the preparation and testing methods should not be substituted for the field sample analytical measurement uncertainty. The laboratory must make an estimation of the matrix interference effects in "real-world" samples and not base their measurement uncertainty estimation on interference-free "reagent-water" samples. Including the estimation of matrix effects provides a realistic and not overly optimistic estimation of measurement uncertainty for field samples. The following table summarizes the uncertainty sources and their corresponding QC samples.

Table C.1: Uncertainty Sources and QC Samples

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
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

Appendix D: Derivations

D.1: Using the GUM Model to Estimate Measurement Uncertainty

First, the standard uncertainty $u(x_i)$ is evaluated for each component x_i of the measurement equation $y = f(x_1, x_2, \ldots x_n)$ where y is the measurement results and y (the dependent variable) is a function of measurement component independent variables $x_1, x_2, \ldots x_n$. Each uncertainty component x_i is represented by an estimated standard deviation, the standard uncertainty, u_i. Next, the estimated uncertainties are combined by a first-order Taylor series approximation of the measurement equation $y = f(x_1, x_2, \ldots x_n)$. The combined standard uncertainty is the square root of the estimated combined variance $u_c^2(y)$. The following equation is the Taylor series expansion for determining the estimated combined variance:

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

Equation D.1

This equation can be simplified to calculate the combined standard uncertainty.

$$u_c^2(y) = \sum_{i=1}^{n} (c_1 u(x_1))^2 + (c_2 u(x_2))^2 + \ldots + (c_n u(x_n))^2 + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} c_i c_j u(x_i) u(x_j) r_{ij}$$

Equation D.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. 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. There are two different approaches for applying the law of propagation of uncertainty. If y is an additive function of $x_1, x_2, \ldots x_n$, then the following equation is used:

$$u_c^2(y) = (c_1 u(x_1))^2 + (c_2 u(x_2))^2 + \ldots + (c_k u(x_n))^2$$

Equation D.3

If $y = x_1 + x_2$ or $y = x_1 - x_2$, then c is equal to 1and the equation can be simplified to Equation D.4:

$$u_c^2(y) = \sum_{i=1}^{n} u(x_i)^2$$

Equation D.4

If y is a multiplicative function of $x_1, x_2, \ldots x_n$, then the following equation is used to determine the relative combined standard uncertainty $u_{c,r}$ where $y \neq 0$ and $|y|$ is the absolute value of y:

$$u_{c,r}^2(y) = (u_c(y)/|y|)^2 = c_1 (u(x_1)/x_1)^2 + c_2 (u(x_2)/x_2)^2 + \ldots + c_n (u(x_n)/x_n)^2$$

Equation D.5

If $y = x_1/x_2$ or $y = x_1 x_2$, then c is equal to 1 and the equation can be simplified to Equation 2.6:

$$(u_c(y)/|y|)^2 = \sum_{i=1}^{n} (u(x_i)/x_i)^2$$

Equation D.6

Last, using a coverage factor k to calculate the expanded uncertainty, $ku_c(y)$ or U of the measurement result y expands the combined standard uncertainty. The value of the coverage factor k is selected because of the confidence level (CL) established. If the probability distribution is normal, or the distribution is assumed to be normal, and the combined uncertainty u_c is a reliable estimate of the standard deviation of y, then $U = 2u_c$ for $k = 2$ results in a confidence level of 95%. The expanded uncertainty U is a function of the confidence level selected and the combined uncertainty u_c of the measurement. The measurement result y is reported with an uncertainty interval $\pm ku_c$ that indicates the probable value of y at the selected confidence level. The relative standard uncertainty, u_r , and the relative combined standard uncertainty, $u_{c,r}$, are related to the relative expanded uncertainty U_r of the measurement result y by the equation $U_r = U/|y|$ where $y \neq 0$, $u_{c,r} = u_c/|y|$, and $U_r = ku_{c,r}$.

In summary, each uncertainty component, x_i, is represented by an estimated standard deviation, s_i, the standard uncertainty, u_i. To calculate the relative uncertainty of the component $u_{i,r}$, each component standard uncertainty, $u(x_i)$, is divided by the component value, x_i, or $u(x_i)/x_i$,. The relative combined standard uncertainty, $u_{c,r}$, is calculated by taking the square root of the sum of the squares of the relative standard uncertainties, $u_c(y)/|y| = (\Sigma(u(x_i)/x_i)^2)^{1/2}$. The relative combined standard uncertainty, $u_{c,r}$, is equal to $u_c(y)/|y|$. The relative expanded uncertainty, U_r, is a product of the relative combined standard uncertainty, $u_{c,r}$, multiplied by a coverage factor. The expanded uncertainty, U, divided by the measurement result y or $U/|y|$, is equal to the relative expanded uncertainty, U_r, where $y \neq 0$ and $U_r = ku_{c,r}$. The relative combined standard uncertainty is expanded by using a coverage factor, k, to calculate the relative expanded uncertainty, $ku_{c,r}(y)$ or U_r, of the measurement result y. If the probability distribution is normal, or is assumed normal, and the relative combined standard uncertainty, $u_{c,r}$, is a reliable estimate of the relative standard deviation of y, then $U = 2u_{c,r}$ when $k = 2$ results in a confidence level of 95%. The relative expanded uncertainty, U_r, is a function of the confidence level selected and the combined uncertainty, $u_{c,r}$, of the measurement. The measurement result y is reported with an uncertainty interval $\pm(y)ku_{c,r}$ that indicates the probability value of y at the selected confidence level.

D.2: Deriving Uncertainty for a Single Test Measurement

The probability that a sample measurement's best estimate result is different from the sample value is represented by the following equation.

$$t_0 = (|x_0 - \eta|)/s$$

Equation D.7

Where t_0 (specific Student's t-variable) is a function of specific sample measurement result (x_0), the sample mean (η), and the sample measurement method standard deviation (s). When replicate measurements of the sample are not made, s must be estimated. The sample mean can only be estimated from the sample measurement result. Therefore, the confidence interval (CI) of η is determined by rearranging Equation D.7 in Equation D.8:

$$CI \text{ of } \eta = x_0 \pm t_0 s$$

Equation D.8

If x_o is an average of replicate sample measurement results, then the standard uncertainty ***(s)*** is used to determine the confidence interval for the sample measurement at a specified confidence level. This is determined by the following equation:

$$CI \text{ of } \eta = X\text{-bar} \pm (t\, s_{X\text{-bar}})/(n)^{1/2}$$

Equation D.9

The term ***X-bar*** is the average of the replicate sample measurement results, $s_{X\text{-bar}}$ is the standard deviation of the data used to calculate ***X-bar***, and ***n*** is the number of measurements. The CI becomes narrower as ***n*** increases. How much the sample measurements mean deviates from the sample mean value is the error of the measurement. This is the determinate or systematic error, and it is approximated by the sample measurement mean with an associated uncertainty interval because the mean is an estimation. The sample value is the average of replicate measurements that approximates the normal distribution around the sample mean, η (not to be confused with the population mean, μ). The standard deviation around the mean is the precision of the measurement. This is the random or stochastic uncertainty.

The difference between the sample mean value and the average of the measurement values is the expanded measurement uncertainty, ***U,*** associated with the sample result is determined by the following equation:

$$U = \eta - X\text{-bar} = \pm((t\, s_{X\text{-bar}})/(n)^{1/2})$$

Equation D.10

The difference between η and ***X-bar*** is expressed as a confidence interval divided by the square root of the number of measurements because it is estimated. The laboratory is confident (at a specified confidence level) that the mean of the sample is within the confidence interval represented by the term $\pm((t\, s_{X\text{-bar}})/(n)^{1/2})$, centered on the mean of the measurements. The interval envelops subsequent calculated means of subsequent measurements and should fall within the $\pm((t\, s_{X\text{-bar}})/(n)^{1/2})$ interval. The uncertainty concerning the sample mean is expressed as a confidence interval in the following equation (Equation 1.16):

$$U = \pm((t\, s_{X\text{-bar}})/(n)^{1/2})$$

Equation D.11

The uncertainty of the measurement mean is therefore an interval of probable values. The larger the number of samples, ***n,*** the narrower the range of probable values becomes. The uncertainty interval of the measurement mean should not be confused with the uncertainty associated with a single test measurement. When a single test measurement is made of an analytical sample, the standard deviation for that test measurement must be estimated from historical data that represents the uncertainty characteristic of the analytical sample.

For single measurement result with an estimated standard deviation, s_E (estimated from appropriate historical quality control data and the nested approach explained in Appendix C), the equation for determining the uncertainty for a single test result is presented in Equation 1.17. The term ***U*** is the uncertainty for a single test result x_o and t_{S_E} is the Student's t-value based the degrees of freedom for the estimated standard deviation, s_E:

$$U \text{ for } x_0 = \pm(t_{S_E}\, s_E)$$

Equation D.12

Appendix E: Examples of the Nested Approach

E.1: Example A: Uncertainty Estimation for a Single Test Measurement

In Example A, the uncertainty is determined for a single test measurement sample. The measurement uncertainty for a single sample measurement cannot be directly calculated, but it can be "backed-out" of the propagation of relative uncertainty equation. Adjusting for systematic error normalizes the measurement result. The relevant component standard uncertainties are combined and expanded to a 99.73% confidence level. Applying the equation for the uncertainty of a single test measurement carries a caveat. The confidence level statement of a single measurement must supported by a control chart or other evidence of statistical control (Taylor, J.K., 28). The control charts used to estimate the single test measurement are the statistical quality control sample data.

Example A: For a data set of 7 individual measurements of a single sample with a mean of 10 μg/L and standard deviation of 1 μg/L, the degrees of freedom, ν, are 6, and a confidence level of 99.7%, the Student's t -value is 4.9. The confidence interval (*CI*) for the mean is represented in the following equation.

$$CI = X\text{-}bar \pm(t\, s/(n)^{1/2})$$

Equation E.1

$$10 \pm (4.9*1) / (7)^{1/2}$$

$$10 \pm 1.8\ \mu g/L$$

For a single test measurement, the standard deviation must be derived by "backing-out" the uncertainty. If the intrinsic instrumental measurement effects (IME) have a relative uncertainty of 1.7%, the method preparation (MPE) has a relative uncertainty of 6.7%, and the matrix interference effects (MIE) have a relative uncertainty of 10%, then the standard deviation can be estimated by the following equation:

$$^{SPL}u_r = ((^{IME}u_r)^2 + (^{MPE}u_r)^2 + (^{MIE}u_r)^2)^{/2}$$

Equation E.2

$$12.2\% = ((1.7\%)^2 + (6.7\%)^2 + (10\%)^2)^{/2}$$

Because the standard deviation is derived from control chart limits, the degrees of freedom are based on 30 measurements used in developing the control limits. For 30 measurements, there are 29 degrees of freedom with a Student's t value of 3.3 for the scalar k coverage factor. The square root of the number of measurements is 1 so the measurement plus or minus the uncertainty becomes $x \pm ts$ (Taylor, J.K., 28). If the sample single test measurement, x, is 10 μg/L, then the following equation calculates the sample value measurement uncertainty interval, y:

$$y = x \pm ts$$

Equation E.3

$$y = 10 \pm (3.3*10*0.12)\ \mu g/L$$
$$y = 10 \pm 4\ \mu g/L$$

Using the nested approach, the single test measurement of the routine field sample has a measurement of 10 μg/L and uncertainty estimated of 4μg/L. The following figure is a graphical presentation of the ratio of the component percent relative standard uncertainties for the intrinsic IME, PME, and MIE.

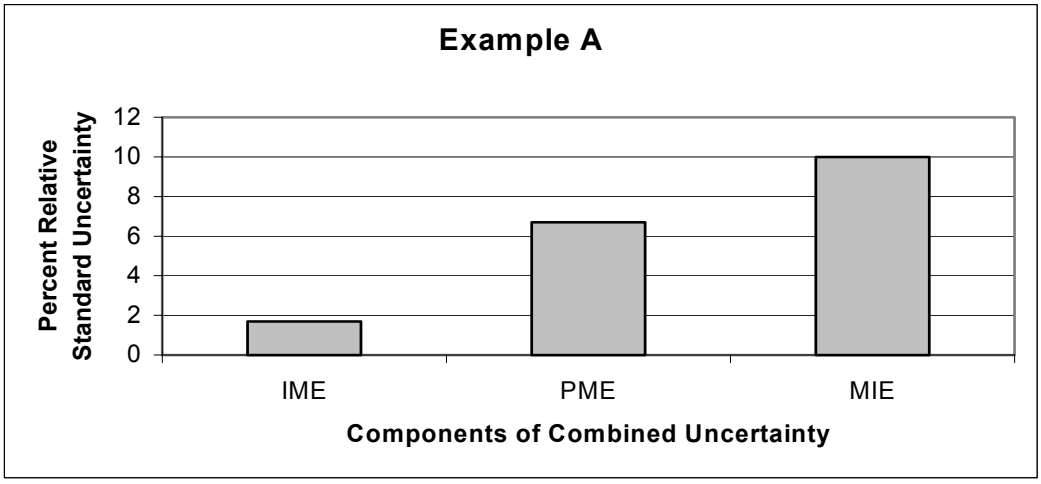


Figure E.1: Example A

The laboratory analysis activities affect these three components, thus they should be included when estimating the laboratory activity contribution to measurement uncertainty.

E.1.1 Correction to the Reference Value

Although the uncertainty associated with sample collection, sample location, and sampling site can be estimated by the nested approach, unless the systematic error for sample collection, sample collection, and sampling site are determined, the population mean cannot be normalized. The laboratory can estimate the systematic error associated with their activities. The following equation is used for calculating the analytical process recovery by multiplying the component sub-process recoveries for sample collection, preparation, and testing:

$$R = R_1 R_2 R_3$$

Equation E.4

This is limited to samples with referenced analyte concentrations, as a confidence interval cannot envelop the systematic uncertainty of a method without a known reference value.

Recovery and correction to the reference value can be conducted for the calibration standard, the ICV, the LCS, and the MSD. By "backing-out" the component recoveries ($R=R_1R_2R_3$) the recovery of the single test measurement of a routine sample can be determined and the sample mean, η, adjusted for laboratory systematic error. However, the field activities systematic error cannot be adjusted. This is because there are no reference values to adjust the field recovery efficiency to, so that μ or the population mean cannot be corrected for systematic error.

The recovery of a single test measurement cannot be measured directly from the subprocesses, but they can be "backed-out" of the multiplicative recovery equation when the accepted concentration is traceable to a reference value. Relative deviation from the accepted value, B_r, is related to relative recovery R_r in the following equation:

$$B_r = (1 - R_r)$$

Equation E.5

For example, if the recovery of the intrinsic instrumental measurement effects are assumed to be equal to the recovery of the instrumental calibration standard analysis (ICS), then the recovery of the spike preparation effects can be "backed-out" of the ICV standard uncertainty.

$$^{ICS}R = {}^{IME}R = 100\%$$

Equation E.6

The spike preparation effect results in a recovery of 100% of the certified spike value. The relative deviation from the accepted value (relative bias) is 0%. The recovery of the ICV is 98%.

$$^{ICV}R = {}^{IME}R\ {}^{SPE}R$$

Equation E.7

$$98\% = 100\% * {}^{SPE}R$$

$$^{SPE}R = 98\%$$

The spike preparation effect results in a recovery of 98% of the certified spike value. The relative deviation from the accepted value (relative bias) is (1-0.98) or 2%. The recovery of the LCS is 95%.

$$^{LCS}R = {}^{IME}R\ {}^{SPE}R\ {}^{PME}R$$

Equation E.8

$$95\% = 100\% * 98\% * {}^{PME}R$$

$$^{PME}R = 97\%$$

The method preparation effect results in a recovery of 97% of the certified spike value. The relative deviation from the accepted value (relative bias) is (1-0.97) or 3%. The recovery of the MIS is 90%.

$$^{MSD}R = {}^{CSE}R\ {}^{SPE}R\ {}^{PME}R\ {}^{MIE}R$$

Equation E.9

$$90\% = 100\% * 98\% * 97\%\ {}^{MIE}R$$

$$^{MIE}R = 95\%$$

The matrix interference effect results in a recovery of 95% of the certified spike value. The relative deviation from the accepted value (relative bias) is (1-0.95) or 5%. When the ICV, LCS, and MS are prepared from the same second source, the recovery can be used to estimate the relative deviation of the accepted value for a single test measurement of a routine sample. If the sample recovery is a combination of the $^{IME}R\ ^{PME}R\ ^{MIE}R$ the sample recovery would be 95%*97%*100% for a sample recovery of 92%. This recovery is an estimation of the recovery and relative systematic error, $B_r = (1 - R)$, of the laboratory activities.

Once the component uncertainties have been "backed-out," the recovery "normalization" factor has been calculated, and the component uncertainties have been "integrated" for the combined standard uncertainty, then the expanded relative uncertainty is determined. If the sample single test measurement is 10 µg/L, the combined recovery is 0.92, the combined relative standard uncertainty is 0.12, and the ***t*** variable is 3.3 for 29 degrees of freedom from the control charts, then the following equation calculates the laboratory uncertainty of the measurement.

$$x = 10/0.92 = 10.9\ \mu g/L$$

Equation E.10

$$x = 10.9 \pm (3.3*10.9*0.12)\ \mu g/L$$

$$x = 10.9 \pm 4.3\ \mu g/L$$

The sample value corrected for systematic error is 10.9 µg/L with an uncertainty of ± 4.3 µg/L from random variation. The sample value is expected to be located within the interval of from 6.6 µg/L to 15.2 µg/L.

E.2: Example B: Sample Collection Effects

Measurement uncertainty is also affected by the field activities. Field-split replicates and co-located replicates are required to estimate the uncertainty attributable to field activities. The results must be above the quantitation limit in order to "back-out" the component uncertainty, and because there is no reference value associated with the field activities, a relative bias cannot be determined. Example B is a collection of field-split duplicate samples. The sample collection standard uncertainty is "backed-out" of the field-split replicates.

Sample collection incorporates locating the planned sample location, collecting the samples, and preserving the samples in the proper container. The sources of uncertainty are "lumped" into the sample collection component. The component uncertainty attributable to sample collection cannot be directly calculated, but it can be "backed-out" of the relative propagation of uncertainty equation. Example B: Ten field-split samples are collected from a site to assess the sample collection process. The relative percent difference equation is used for duplicate results to assess the quality of the measurements. The following is the relative percent difference, *RPD*, equation:

$$RPD = \frac{Field\ Sample - Duplicate\ Sample}{\frac{1}{2}(Field\ Sample + Duplicate\ Sample)} * 200$$

Equation E.11

This equation does not provide the standard deviation required to calculate the uncertainty. The standard deviation of duplicate results from different samples is calculated using the following equation:

$$s = (\sum(d^2)/2k)^{1/2}$$

Equation E.12

The following table is the result of the field and field-split replicate sample analysis.

Table E.1

Field Sample, mg/kg Copper	Field-Split Sample, mg/kg Copper	Difference Between Duplicates	Square of Differences
32	30	2	4
38	32	6	36
29	32	3	9
24	34	10	100
33	30	3	9
33	25	8	64
34	34	0	0
26	29	3	9
35	33	2	4
34	37	3	9

The standard deviation between duplicates for the 10 field and field-split duplicates is 3.5 mg/kg. However, the relative standard deviation between duplicates is needed to "back-out" the uncertainty attributable to sample collection field activities.

The following modified equation is a special application of the standard deviation of duplicate results equation. The relative difference between duplicates, d_r (difference divided by average of duplicates,) and the square of the relative difference between duplicates was calculated to determine the relative standard deviation, s_r :

$$s_r = (\sum(d_r^2)/2k)^{1/2}$$

Equation E.13

The following table presents the data used to determine the relative standard deviation:

Table E.2

Field Sample, mg/kg Copper	Field-Split Sample, mg/kg Copper	Mean of Duplicates, mg/kg Copper	Relative Difference Between Duplicates	Square of Relative Difference Between Duplicates
32	30	32.5	0.062	0.0038
38	32	35	0.171	0.0294
29	32	31.5	0.095	0.0091
24	34	29	0.345	0.1189
33	30	31.5	0.095	0.0091
33	25	29	0.276	0.0761
26	29	27.5	0.109	0.0119
34	34	34	0.000	0.0000
34	33	33.5	0.030	0.0009
35	37	36	0.056	0.0031

The relative standard deviation (RSD) between duplicates is 11.4% rounded to 11% for significant figures. If the intrinsic measurement effects, the matrix interference effects, and the sample preparation effects are known, then the sample collection effects can be determined. At the 99% confidence level, the confidence interval of the normal sample mean is from 31.5 to 32.5 mg/kg. This indicates that the sample site contamination is homogenous. The relative sample collection effects uncertainty is "backed-out" of the following equation:

$$({}^{FSR}u_r)^2 = ({}^{IME}u_r)^2 + ({}^{PME}u_r)^2 + ({}^{MIE}u_r)^2 + ({}^{SCE}u_r)^2$$

Equation E.14

For this example, the intrinsic instrumental relative standard uncertainty is 1%, method preparation relative standard uncertainty is 7%, the matrix interference effects relative standard uncertainty is 7%, and the relative combined uncertainty of the field-split replicate sample is 11%.

$$(11\%)^2 = (1)^2 + (7)^2 + (7)^2 + ({}^{SCE}u_r)^2$$

$${}^{SCE}u_r = 6\%$$

The relative uncertainty attributable to the sample collection effects is 6%. The ratio of IME: PME: MIE: SCE (1:7:7:6) indicates that the measurement uncertainty is affected less by the sample collection effects (SCE) than by the sample preparation or matrix interference effects. The following figure is a graphical presentation of the IME, PME, MIE, and SCE.

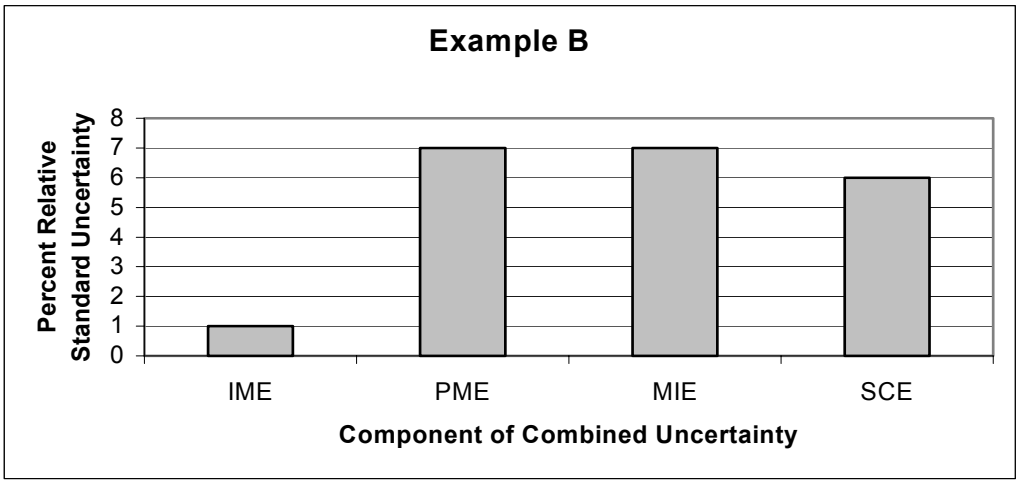


Figure E.2: Example B

The mean of the 20 measurements (not correlated as field and field-split) was 31.7 mg/kg and the standard deviation for the 20 measurements was 3.7 mg/kg. This indicates that there is very little variation between the field and field-split replicate samples (sample collection effects) and that there is very little variation between the field samples from different locations (sampling site effects). The mean contaminant level and standard deviation for the collection of results indicate that the distribution of the contaminant is relatively uniform for the site. However, because co-located replicate samples were not included in the analysis, there is a potential that "spikes" or "hot-spots" were not detected. The frequency between sampling events may not have captured "spikes" in the contamination concentration or the spatial distribution of samples may not have captured "hot-spots." To determine the efficacy of the sampling strategy, co-located samples must be collected.

E.3: Example C: Sampling Site Effects: "Hot Spots"

Sampling strategies are designed to capture the representative contaminant concentration of the environmental site, estimate stratified distribution of the contaminant, or identify "hot-

spots." Geostatistical methods are useful for interpolation of contaminant concentration between sampling points. Co-located samples can be used to evaluate the accuracy of the interpolation. Example C is a collection of co-located duplicate samples. The sample location standard uncertainty is "backed-out" of the co-located replicates.

Temporal and spatial sampling strategies include periodic sampling, simple random sampling, stratified random sampling, cluster sampling, systematic grid sampling, and random sampling within grids. Sample collection design uncertainties are attributed to inadequacy of the design to capture the complete extent of variability that exists for the contaminant distribution in the sample site. It is impossible to measure the contaminant level at every point in space and time; therefore, sampling plans are incomplete to some degree. Because it is impossible to know with complete certainty the contaminant level at locations that are not measured, sample collection results in uncertainty. The greater the natural or inherent variation in contaminant levels, the greater the uncertainty associated with the decision based on the sample results. The uncertainty is in the representativeness of the level of contamination at the sample site.

Repetitive test measurements of the same sample reduces the uncertainty of the sample mean, η, but does not reduce the uncertainty associated with the population mean, μ. To reduce the uncertainty associated with the population mean, multiple samples must be collected. Each sample is representative of the sample location area from which it is collected. The representativeness of the sample can be evaluated by co-located samples.

Example C: From a site, 13 field co-located replicate samples are collected to estimate the localized site variation and assess the sampling strategy. The relative standard deviation of the 13 field/co-located sample replicates is calculated. The results of the sample analysis are presented in the following table:

Table E.3

Field Sample, mg/kg Chromium	Field Co-Located Sample, mg/kg Chromium	Mean of Duplicates, mg/kg Chromium	Relative Difference Between Duplicates	Square of Relative Difference Between Duplicates
13	12	12.5	0.080	0.0064
19	15	17	0.235	0.0554
14	15	14.5	0.069	0.0048
17	16	16.5	0.061	0.0037
13	157	85	1.694	2.870
11	120	65.5	1.664	2.777
15	13	14	0.429	0.0204
18	180	99	1.636	2.678
94	11	52.5	1.581	2.499
11	17	14	0.429	0.1837
15	13	14	0.143	0.0204
18	19	18.5	0.054	0.0029
16	19	17.5	0.171	0.0294

The relative standard deviation, s_r, is calculated from the relative difference, d_r, between duplicates. The relative difference is the difference between duplicates divided by the mean of the duplicates. The difference between the original and duplicate, d, is divided by the mean of the original and duplicate for the relative difference, d_r the relative difference is squared, summed, divided by two times the number of samples, k, and then the square root is taken. The relative standard uncertainty of the co-located samples is used to "back-out" the sampling site effects on measurement uncertainty.

The relative standard deviation (RSD) between duplicates is 65%. If the intrinsic measurement effect RSD is 2%, the sample preparation effects RSD is 10%, the matrix

interference effect RSD is 10%, and the sample collection effect RSD is 10%, then the sampling site effects can be calculated. The measurement uncertainty attributable to the sampling strategy is calculated using the propagation of uncertainty equation. The relative sample location effects (SLE) uncertainty is "backed-out" of the following equation:

$$({}^{CLR}u_r)^2 = ({}^{IME}u_r)^2 + ({}^{PME}u_r)^2 + ({}^{MIE}u_r)^2 + ({}^{SCE}u_r)^2 + ({}^{SLE}u_r)^2$$

Equation E.15

$$(65\%)^2 = (2)^2 + (10)^2 + (10)^2 + (10)^2 + ({}^{SLE}u_r)^2$$

$${}^{SLE}u_r = 63\%$$

The total relative uncertainty of the field co-located replicate samples is 63%. The ratio of IME: PME: MIE: SCE: SLE (2:10:10:10:63) indicates that the uncertainty of the measurement is significantly affected by the site contamination distribution. In this example, there was significant measurement disparity associated with both the co-located replicate samples and the site contamination distribution. The co-located replicate samples indicate that the site has "hot-spot" contamination. The site contamination distribution effects "swamp" the other contributing effects on uncertainty. The most effective way to reduce the uncertainty associated with these measurements is to develop a sampling plan that reduces uncertainty associated with the sampling site. The following figure is a graphical presentation of the component ratios of the intrinsic IME, PME, MIE, SCE, and SLE.

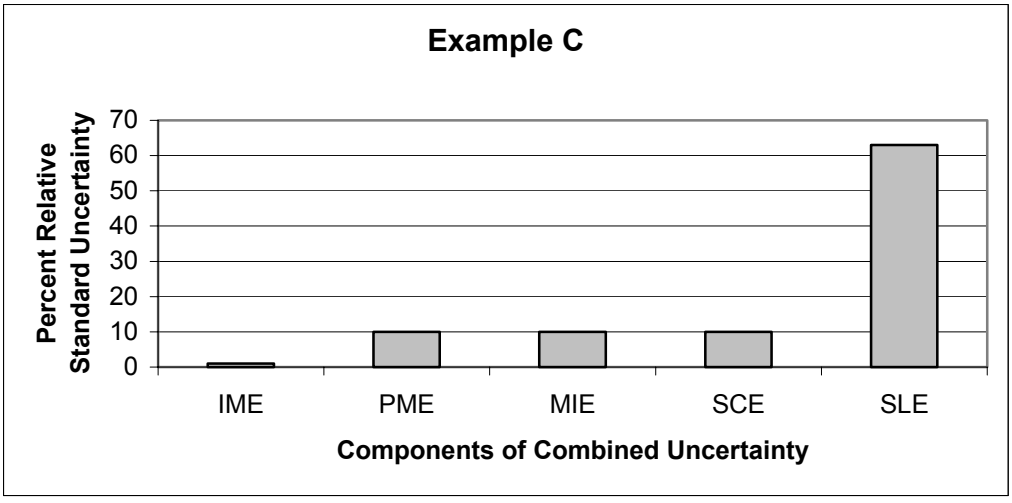


Figure E.3: Example C

The uncertainty attributable to the sample location area is significantly higher than the other sources of uncertainty because several of the field/co-located results are significantly different. This is indicative of "hot-spot" contamination. Therefore, a "hot-spot" sample strategy should be used to evaluate the contaminant distribution. This would require a second round of collecting samples. Combining samples from different sample locations to form composite samples is discouraged for heterogeneous media because the combining process makes it harder

to identify "hot-spots." Compositing samples averages out the disparate contaminant levels and mask "hot-spots." The use of co-located replicate field samples improves the probability of detecting "hot-spot" contamination that has an area diameter less than the sampling interval. Representative samples are difficult to achieve when the site contamination is heterogeneous (stratified or "hot-spots"). Under this circumstance, a larger number of samples are required to calculate representative contamination concentrations, or map contaminant strata and "hot-spots."

E.4: Example D: Sampling Site Effects: Gradient Distribution

In example D the contaminant distribution effects are examined by the use of co-located replicate samples using the nested approach. The IME, PME, and MIE are estimated from the quality control limits of the instrument calibration standard, laboratory control sample, and the matrix sample. The following are the relative standard uncertainties associated with the laboratory measurement activities: IME = 2%, PME = 4%, and MIE = 6%. The relative standard uncertainty from duplicate field-split (FSR) samples is 8%. The result cannot be normalized to adjust for systematic error attributable to the field sampling activities unless the bias is determined or estimated. Example D: Co-located field samples are collected with the twenty original field samples. The following table is a summary of the co-located analytical results:

Table E.4

Sample Identification	Field Sample, mg/kg	Field Co-Located Sample, mg/kg	Mean of Duplicates, mg/kg	Relative Difference Between Duplicates	Square of Relative Difference Between Duplicates
D-01	14	13	13.5	0.074	0.00549
D-02	19	15	17	0.235	0.05536
D-03	15	16	15.5	0.065	0.00416
D-04	18	17	17.5	0.057	0.00327
D-05	17	13	15	0.267	0.07111
D-06	15	11	13	0.308	0.09467
D-07	20	25	22.5	0.222	0.04938
D-08	26	23	24.5	0.122	0.01499
D-09	30	34	32	0.125	0.01563
D-10	36	42	39	0.154	0.02367
D-11	39	38	38.5	0.026	0.00067
D-12	32	25	28.5	0.246	0.06033
D-13	24	21	22.5	0.133	0.01778
D-14	17	13	15	0.246	0.07111
D-15	14	18	16	0.250	0.06250
D-16	15	11	13	0.308	0.09467
D-17	16	17	16.5	0.061	0.00367
D-18	17	13	15	0.267	0.07111
D-19	14	18	16	0.250	0.06250
D-20	16	19	17.5	0.171	0.02939

The relative standard deviation (RSD) between duplicates is 14%. The intrinsic measurement effect RSD is 2%, the sample preparation effects RSD is 4%, the matrix interference effect RSD is 6%, and the sample collection effect RSD is 8%. The measurement uncertainty attributable to the site variability is calculated using the propagation of uncertainty equation. The relative sampling strategy effects (SSE) uncertainty is "backed-out" of the following equation:

$$({}^{CLR}u_r)^2 = ({}^{IME}u_r)^2 + ({}^{PME}u_r)^2 + ({}^{MIE}u_r)^2 + ({}^{SCE}u_r)^2 + ({}^{SLE}u_r)^2$$

Equation E.16

$$(14\%)^2 = (2)^2 + (4)^2 + (6)^2 + (8)^2 + ({}^{SLE}u_r)^2$$

$${}^{SLE}u_r = 9\%$$

The total relative uncertainty of the field co-located replicate samples is 9%. The ratio of IME: PME: MIE: SCE: SLC (2:4:6:8:9) did not indicate "hot-spot" contamination. The sampling strategy effectively captured the contaminant distribution of the site. The following figure is a graphical presentation of the component ratios of the IME, PME, MIE, SCE, and SSE.

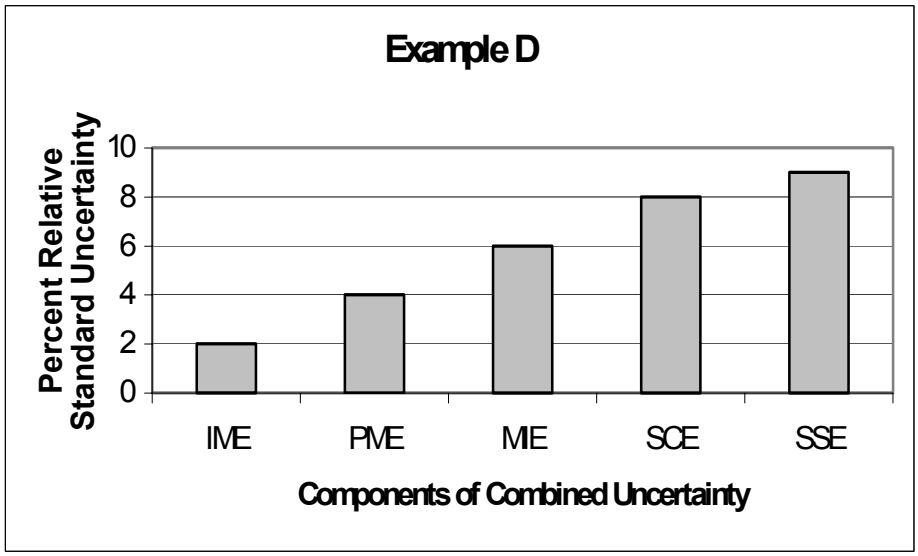
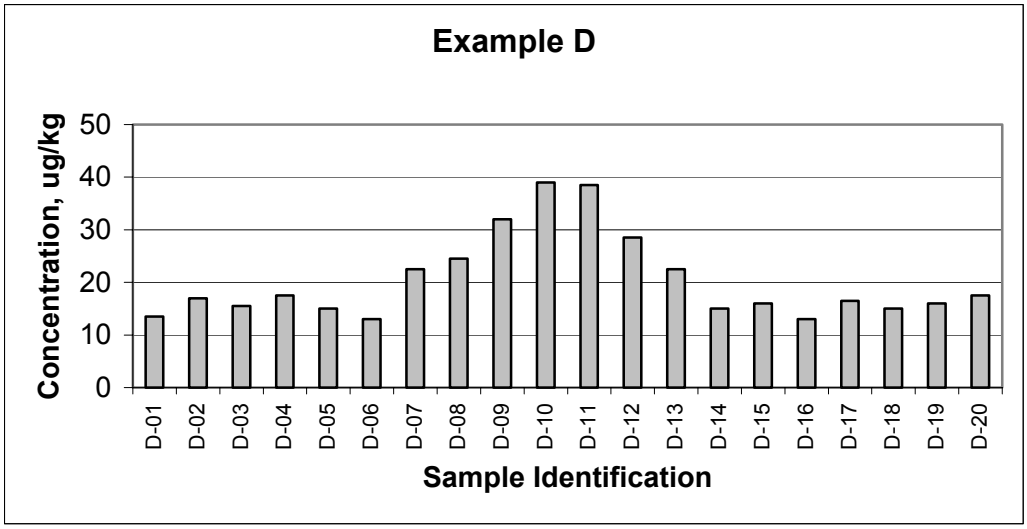


Figure E.4: Example D

This "stair-step" pattern indicates that there is not a significant "single-component" contribution to sampling and measurement uncertainty. The following is another graphical presentation of the results of Example D. The samples were taken as a single-transect of the environmental site of an initial survey of the site.

Figure E.5



In this example, the relative standard deviation of the routine field samples (RFS) collected from the site is 20%. The sample media contamination effects (SME) for the sample site is "backed-out" of the following equation:

$$({}^{RFS}u_r)^2 = ({}^{IME}u_r)^2 + ({}^{PME}u_r)^2 + ({}^{MIE}u_r)^2 + ({}^{SCE}u_r)^2 + ({}^{SLE}u_r)^2 + ({}^{SME}u_r)^2$$

Equation E.17

$$(20\%)^2 = (2)^2 + (4)^2 + (6)^2 + (8)^2 + (9)^2 + ({}^{SME}u_r)^2$$

$${}^{SME}u_r = 14\%$$

The following table presents the uncertainty budget for example D. Each component that contributes to uncertainty is in the uncertainty budget.

Table E.5 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
Matrix Interference Effects	MIE	6%	Normal or Lognormal	1	3
Sample Collection 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

The probability distribution is assumed normal for the IME and PME. The MIE, SCE, SSE, and SME probability distributions are assumed normal or lognormal. Lognormal distributions indicate "hot-spots" or hot particles in samples with significantly elevated contaminant analyte levels above the average level. The sensitivity coefficient is 1 because the components are modeled as multiplicatively combined. The relative uncertainty contribution is a ratio of the component relative standard uncertainties. For the example, the ratio of MIE:SCE:SSE:SME is 1:2:3:4:4.5:7.

E.5: Example E: Radioanalytical Recovery Efficiency

Measurement of radioactivity is an example of the multiplicative functional relationship of analytical components. The laboratory analytical process is broken down into sample preparation that results in a particular chemical yield or recovery of the radioanalyte and the instrumental counting that results in a particular counting efficiency or recovery of decay events. Radioanalytical measurement requires calculations that include sample preparation chemical yield, y, radioactive ingrowth factor, i, radioactive decay factor, d, units conversion factor, u, volumetric or gravimetric units, v or g, and counting recovery efficiency, e, to transform a net counting rate, R_{net}, to a radioactivity measurement, C. The background counting rate is subtracted from the gross counting rate for the net counting rate:

$$R_{net} = R_{gross} - R_{background}$$

Equation E.18

The following equation is the general form for calculating radioactivity from the net counting rate:

$$C = R_{net} / (e\ y\ i\ v\ d\ u)$$

Equation E.19

The recovery efficiency of a radioactive counting instrument is the ratio of the counting rate, ***cpm*** or counts per minute, and the disintegration rate, ***dpm*** is disintegration per minute**.** Equation E.20 represents this relationship.

$$R = cpm/dpm$$

Equation E.20

This is equivalent to the following equation:

$$R = cpm * 1/dpm$$

Equation E.21

For example, the certified reference value for a certain radioactive source is 1000 dpm. The Poisson distribution is the model used to describe radioactive disintegration and counting. The normal distribution is related to the Poisson distribution because the Poisson distribution approximates a normal distribution at greater than 20 measurements. This approximation is appropriate for ***n*** greater than or equal to 20 where ***n*** is a large number of decay events.

For this special case of the normal distribution, the standard deviation is equal to the square root of the mean (the mean and variance are equal) that approximates the Poisson distribution. At the 95% confidence level (CL) the uncertainty in dpm is $(1000)^{1/2}$ times 2 or 63 dpm. The disintegrations per minute rate is 1000 ± 63 dpm. The expanded uncertainty interval is from 937 to 1063 dpm. The probability is 0.95 for the analyte value to be within the uncertainty interval. The radioactive source was counted for 1 minute with a count rate of 600 cpm. At the 95% confidence level, the uncertainty was 49 cpm. The count per minute is 600 ± 49 cpm. The counting efficiency or recovery efficiency is the ratio of ***cpm/dpm*** and the combined standard uncertainties of the ***cpm*** and the ***dpm.*** Because the efficiency is multiplicative and because the two variables are statistically independent, the propagation of relative uncertainty is determined by the following equation:

$$^{R}U_r = (({}^{cpm}U/cpm)^2 + ({}^{dpm}U/dpm)^2)^{1/2}$$

Equation E.22

A capital ***U*** is used to symbolize uncertainty because the combined standard uncertainty was expanded to the 95% confidence level. The recovery efficiency combined with the relative uncertainties of cpm and dpm are determined by the following equation:

$$R = (cpm/dpm) \pm U$$

Equation E.23

Using Equation 3.21, the recovery efficiency with relative uncertainty is calculated in the following equation:

$$R = (600cpm/1000dpm) \pm (600cpm/1000dpm)\ [(49cpm^2/600cpm^2) + (63dpm^2/1000dpm^2)]^{1/2}$$

Dividing the rate uncertainty by the rate results in the relative expanded standard uncertainties for the cpm and dpm:

$$R = 0.60 \pm 0.60\ ((0.082^2) + (0.063^2))^{1/2}$$

Equation E.24
The relative expanded uncertainty of the recovery, ${}^{R}U_r$, is calculated in the following equation:

$$ {}^{R}U_r = ((0.082^{2}) + (0.063^{2}))^{1/2} = 0.10 $$

Equation E.25
The recovery efficiency at the confidence level of 95% is presented in the following equation:

$$ R = cpm/dpm = 0.60 \pm (0.60 * 0.10) = 0.60 \pm 0.06 $$

Equation E.26
The counting efficiency 0.6 has an uncertainty interval ± 0.06. The confidence interval at 95% confidence level is 0.54 to 0.66. The uncertainty is the relative expanded uncertainty of the recovery, ${}^{R}U_r$. For a multiplicative combination, the relative expanded uncertainty is determined. The recovery can be multiplied by 100 for the percent recovery, ***%R*** from 54% to 66%. Approximately 95% of the time the recovery falls between 54% and 66% efficiency. Once the counting efficiency is calculated, the cpm measurement of a sample is used to calculate the dpm sample results. If the cpm of a sample is 50 ± 14 cpm at the 95% CL, and the calculated recovery efficiency is 0.60 ± 0.06, then the dpm of the sample is calculated using the following equation:

$$ R = cpm/dpm $$

Equation E.27
Replacing the symbols with known values results in the following equation:

$$ 0.60 \pm 0.06 = 50 \text{ cpm}/x \text{ dpm} \pm 50 \text{ cpm}/x \text{ dpm} \left[(14\text{cpm}/50 \text{ cpm})^{2} + ({}^{x}U/x \text{ dpm})^{2} \right]^{1/2} $$

Equation E.28
The dpm is "backed-out" of the equation to calculate the sample results when the recovery efficiency and cpm are known. The unknown ***x*** dpm and relative uncertainty of ***x***, ${}^{x}U$, are solved by rearranging and simplifying the equation:

$$ x \text{ dpm} \pm {}^{x}U \text{ dpm} = 50\text{cpm}/0.60 \pm ((14\text{cpm}/50 \text{ cpm})^{2} + (0.06/0.60)^{2})^{1/2} $$

Equation E.29
The equation is split up into two parts, ***x dpm*** and $\pm x \text{ dpm} * {}^{x}U_r$ and the relative uncertainty of ***x***, ${}^{x}U_r$. The relative uncertainty of ***x*** is the ratio of ${}^{x}U \text{ dpm}/x \text{ dpm}$.
The technique of **splitting** the equation and determining the relative uncertainty of ***x,*** simplifies the calculations. Equation 3.30 normalizes the cpm to account for systematic error:

$$ x \text{ dpm} = 50 \text{ cpm}/0.60 $$

Equation E.30
The following equation is used to estimate the uncertainty:

$$ {}^{x}U_r \text{ dpm} = x \text{ dpm} ((14\text{cpm}/50 \text{ cpm})^{2} + (0.06/0.60)^{2})^{1/2} $$

Equation E.31
The sample results are calculated by using the following equation:

$$ \text{Sample results} = x \text{ dpm} \pm (x \text{ dpm} * {}^{x}U_r) $$

Equation E.32

Solving for ***x*** dpm separately from the ${}^{x}U_r$ in the following equation normalizes the counting rate to the disintegration rate. When the result is normalized the uncertainty associated with the systematic error correction must also be incorporated in the calculations:

$$x\ dpm = 50\ cpm/0.60 = 83\ dpm$$

Equation E.33

After solving for ***x*** dpm, the relative uncertainty for ***x*** $({}^{x}U_r)$ is solved by "backing-out" the unknown uncertainty:

$${}^{x}U_r = ((0.28)^2 + (0.10)^2)^{1/2}$$

Equation E.34

Squaring the relative uncertainties results in the following equation:

$${}^{x}U_r = ((0.0784) + (0.01))^{1/2}$$

Equation E.35

Adding the squares and taking the square root of the sum of the squares results in the following equation:

$${}^{x}U_r = 0.297$$

Equation E.36

The value 0.297 multiplied by 100 results in a 29.7% percent relative expanded uncertainty for the ***x*** dpm. The sample results are calculated by the following equation:

$$Sample\ results = 83\ dpm \pm (83dpm * 0.297) = 83\ dpm \pm 24\ dpm$$

Equation E.37

Splitting the equation, "backing-out" the relative uncertainty, and normalizing the measurement results are used for estimating measurement uncertainty and correcting systematic error. The preparation and counting components are combined multiplicatively to determine the recovery of the analyte for the sample. For example, if the extraction step were 95% efficient, the separation step were 95% efficient, and the concentration step were 95% efficient, then the carrier recovery would be 86% (95%*95%*95% = 86%). Using the general radioanalytical equation, the sample preparation recovery (chemical yield) and the sample counting recovery (counting efficiency) are multiplied together. If the carrier precipitate chemical recovery is 86% and the counting efficiency is 50%, then the counts per minute are divided by the product of 0.86 multiplied by 0.50 (along with the constant factors of ingrowth, decay, and conversion) to determine the disintegrations per minute. This demonstrates that the sample preparation recovery and the sample testing recovery are multiplicatively combined.

E.6: Example F: Trace Metals Data from Quality Control Samples

The summary statistics presented in the Tables E.6 for copper of the quality control samples are presented to illustrate the type of data that an environmental laboratory has available to carry out the nested approach to measurement uncertainty and correct measurement bias to the sample value. The relative standard deviation for each quality control sample is used to "back-out" analytical component standard uncertainties.

Table E.6: Instrumental Calibration using a Copper Standard

Certified Concentration, mg/L	Reanalysis Measurement, mg/L	Difference Between Reference Value and Measured Value, mg/L	Relative Percent Difference
1.00	0.99	0.01	1
1.00	1.00	0.00	0
1.00	0.97	0.03	3
1.00	1.00	0.00	0
1.00	1.01	0.01	1
1.00	1.03	0.03	3
1.00	1.01	0.01	1
1.00	1.00	0.00	0
1.00	0.99	0.01	1
1.00	1.00	0.00	0
1.00	1.03	0.03	3
1.00	1.01	0.01	1
1.00	0.97	0.03	3
1.00	1.00	0.00	0
1.00	0.99	0.01	1
1.00	1.01	0.01	1
1.00	1.01	0.01	1
1.00	0.98	0.02	2
1.00	1.03	0.03	3
1.00	1.00	0.00	0
1.00	0.97	0.03	3
1.00	1.02	0.02	2
1.00	1.00	0.00	0
1.00	0.99	0.01	1
1.00	1.02	0.02	2
1.00	1.00	0.00	0
1.00	0.99	0.01	1
1.00	0.98	0.02	2
1.00	1.00	0.00	0
1.00	0.99	0.01	1

This table presents measurement results for an ICS reanalysis from 30 different batches. Trace metals are tested by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Running a calibration blank to zero the instrument and an instrument calibration standard standardizes the ICP. The instrument calibration standard (ICS) has a 1-mg/L concentration of trace metals including copper. The calibration blank and the calibration standard are reanalyzed. The reanalysis is one of the techniques used to verify that the ICP is properly standardized and that the instrument is in statistical control. A statistical analysis of recovery data for copper was conducted to establish statistical quality control limits. The data was plotted to determine whether a trend in the data was developing. The results formed a "saw-tooth" pattern indicating that no significant trend in the data as seen in the following figure.

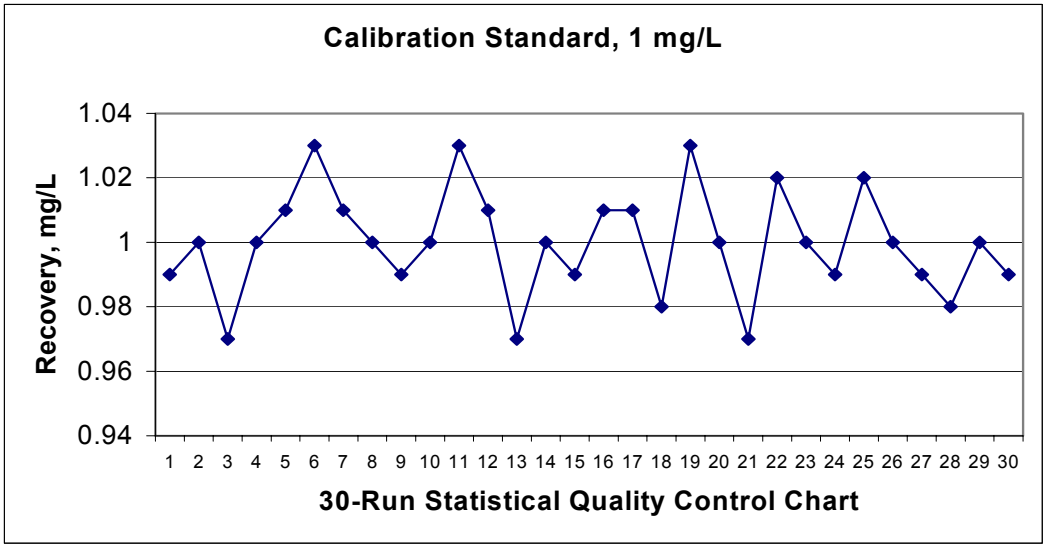


Figure E.6: Copper Instrumental Calibration Standard (ICS)

The following table is a summary of the statistical quality control limits data from Table 3 as well as quality control limits for ICV, LCS, and MS/MSD recovery.

Table E.7: Statistical Quality Control Limits

Quality Control Sample	Certified Standard Value, mg/L	Standard Deviation, mg/L	Measurement Mean, mg/L	Coefficient Of Variation	Relative Standard Deviation
ICS Recovery	1.0	0.017	1.00	0.017	1.7%
ICV Recovery	0.50	0.017	0.490	0.033	3.3%
LCS Recovery	0.50	0.032	0.475	0.067	6.7%
MS/MSD Recovery	0.50	0.047	0.450	0.10	10%

The following table lists typical statistical quality control limits for quality control samples where the control limit is 3-sigma (99.73% CL).

Table E.8: Statistical Quality Control Limits with a limit of 3-sigma

Quality Control Sample	Percent Recovery Limits (Lower and Upper Limits)	Bias (%)	Precision (%)
Calibration Standard Reanalysis Check	95 – 105	0	±5
Independent Calibration Verification	88-108	-2	±10
Laboratory Control Sample (LCS)	75-115	-5	±20
Matrix Spike/Matrix Spike Duplicate Sample	60 – 120	-10	±30