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U.S. Environmental Protection Agency
Science and Ecosystem Support Division
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OPERATING PROCEDURE

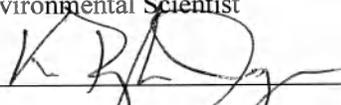
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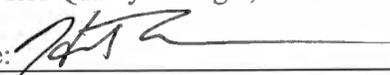
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Revision History

The top row of this table shows the most recent changes to this controlled document. For previous revision history information, archived versions of this document are maintained by the SESD Document Control Coordinator on the SESD local area network (LAN).

History	Effective Date
<p>SESDPROC-014-R2, Field Measurement Uncertainty, replaces SESDPROC-014-R1.</p> <p>Cover Page: SESD’s reorganization was reflected in the authorization section by making John Deatrck the Chief of the Field Services Branch. The FQM was changed from Bobby Lewis to Hunter Johnson.</p> <p>Revision History: Changes were made to reflect the current practice of only including the most recent changes in the revision history.</p> <p>General: Corrected any typographical, grammatical and/or editorial errors.</p> <p>Section 2.2: The following was added to the third sentence: “representativeness of the sample”</p> <p>Section 3.3: Equation 6 was updated.</p>	<p>March 23, 2016</p>
<p>SESDPROC-014-R1, Field Measurement Uncertainty, replaces SESDPROC-014-R0.</p>	<p>April 30, 2012</p>
<p>SESDPROC-014-R0, Estimating Field Measurement Uncertainty, Original Issue</p>	<p>February 11, 2008</p>

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1 General Information

1.1 Purpose

The purpose of this procedure is to provide direction regarding reporting uncertainty of field measurements.

1.2 Scope/Application

Environmental field measurements pose unique challenges for estimating measurement uncertainty. This procedure addresses these uncertainty issues related to field measurements and field instrumentation and provides a methodology for estimating uncertainty for environmental measurements conducted in the field by SESD investigators. See Section 3 of this procedure for more detail on the issues associated with estimating uncertainty for environmental field measurements and the methodologies employed by SESD for estimating field measurement uncertainty. Uncertainty statements can only be made for data collected following the initial effective date of this operating procedure. Mention of trade names or commercial products in this procedure does not constitute endorsement or recommendation for use.

1.3 Documentation/Verification

This procedure was prepared by persons deemed technically competent by SESD management, based on their knowledge, skills and abilities. The official copy of this procedure resides on the SESD local area network (LAN). The Document Control Coordinator is responsible for ensuring the most recent version of the procedure is placed on the LAN and for maintaining records of review conducted prior to its issuance.

1.4 Definitions

1.4.1 Accuracy of measurement (Accuracy)

Closeness of the agreement between the result of a measurement and the true value of the analyte being measured; where the true value is often theoretical or unknowable. Accuracy is a function of both precision and bias.

1.4.2 Precision

With respect to a single device, put into operation repeatedly without adjustments, *precision* is the ability to produce the same value or result, given the same input conditions and operating in the same environment. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

1.4.3 Bias

Consistent deviation of measured values from the true value, caused by a systematic error, or by two or more such errors operating cumulatively.

1.4.4 Qualitative Measurement

Detection techniques used to identify the compounds or physical properties associated with the sample.

1.4.5 Quantitative Measurement

Measurement techniques used to determine the amount of each compound or the amount of the physical property associated with the sample.

1.4.6 Detection Limits

The lowest concentration or amount of target analyte that can be identified, measured, and reported with confidence that the analyte concentration is not a false positive.

1.4.7 Standard Deviation

A measure of how much the data in a sample population are scattered around its mean value. It is usually denoted with the letter σ (lower case sigma). A standard deviation is defined as the square root of the variance.

1.4.8 Significant

Having an outcome unlikely to be caused by chance, and therefore indicating a systematic relationship, between measurements and conditions.

1.5 References

Analytical Support Branch Laboratory Operations and Quality Assurance Manual, most recent version.

International Organization for Standardization (ISO). (1993, corrected and reprinted 1995). *Guide to the Expression of Uncertainty in Measurement* (GUM).

International Organization for Standardization (ISO). (1993, second edition). *International Vocabulary of Basic and General Terms in Metrology*.

National Enforcement Investigations Center Operating Procedure for Estimation of Measurement Uncertainty (NEICPROC/07-004), November 9, 2007.

National Institute for Standards and Technology (NIST). (1994). *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results* (TN-1297).

National Institute for Standards and Technology (NIST). (October 2000). *Essentials of Expressing Measurement Uncertainty*. Retrieved February 28, 2007 from <http://www.physics.nist.gov/cuu/Uncertainty/index.html>

SESD Operating Procedure for Logbooks (SESDPROC-010), most recent version.

SESD Table of Field Measurement Uncertainties (SESDFORM-034), most recent version.

William J. Tilstone, "Uncertainty of Measurement," *The FQS Update*, vol. 2, issue 2 (June 2007), pages 1-3.

2 Methodology

2.1 General

ISO/IEC 17025:2005 requires reporting of measurement uncertainty for quantitative analytical results under three conditions:

- 1) when uncertainty is relevant to the validity or application of a measurement method,
- 2) when a customer's instruction so requires,
- 3) when the uncertainty affects compliance to a regulatory limit.

Uncertainty statements are typically requested by the customer in the planning phase of a project. If a customer requests an uncertainty statement following completion of the project, SESD management will determine whether it is feasible to report the uncertainty. For field data appearing in reports, uncertainty should be calculated and reported for data that directly affects compliance to a regulatory limit. For data collected as indicator parameters, (e.g. measurements to verify stabilization of a monitoring well or to develop strata for sample collection) uncertainty statements will not be reported unless the customer requests it or Project Leader deems it necessary.

The overall goal of documenting measurement uncertainty is to provide information that can be used for decision making. To achieve this goal, it is important to know if measurement uncertainty related to detection limits, field analytical bias, lack of precision and susceptibility to interferences is significant.

2.2 Uncertainty Contributors

Both qualitative and quantitative factors contribute to field measurement uncertainty. For field measurements, there are several factors that can affect qualitative and quantitative measurements. Qualitative uncertainty factors include but are not limited to interferences, environmental conditions, sample handling, representativeness of the sample and instrument maintenance and operation. The SESD field branches reduce the impact of qualitative uncertainty factors through standard operating procedures that address the previously mentioned factors when possible. To date, a uniform approach to estimating the uncertainty associated with qualitative uncertainty contributors has not been developed by the scientific community. Qualitative uncertainty factors that are not addressed through standard operating procedures (e.g., weather extremes and any potential impact they may have had on the data) are discussed in the final report of a project.

The amount of uncertainty contributed by quantitative uncertainty factors can typically be determined. However, it is important to note that qualitative uncertainty factors can also

impact quantitative uncertainty factors. Quantitative uncertainty factors include, but are not limited to, calibration, sample matrix, environmental conditions, sample handling and equipment maintenance and operation. Factors that are known to affect quantitative uncertainty are instrument precision and accuracy, and the accuracy of calibration standards. Field investigators should be aware of inherent instrument limitations, such as potential interferences, detection limits, and accuracy, and should ensure that the instrument is capable of collecting data that satisfies the data quality objectives of the study, particularly for studies that involve regulatory limits.

2.3 Reporting Uncertainty Statements

Uncertainty statements will be reported in accordance with the guidance presented in the International Organization for Standardization (ISO) *Guide to the Expression of Uncertainty in Measurement* (GUM) or other adapted references based on the GUM. The National Institute for Standards and Technology (NIST) *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results* (NIST Technical Note 1297) is a helpful aid for understanding the GUM. For a complete listing of references for this procedure see Section 1.5.

In addition to the procedures defined here, if an uncertainty statement is reported, SESD investigators will consult the GUM, NIST or other adapted references in order to specifically evaluate how to use quoted uncertainties to derive and report standard uncertainty for a particular field measurement. See Section 2.1 of this procedure for a list of when uncertainty statements are reported.

2.4 Estimating Quantitative Uncertainty

When estimating field measurement uncertainty, field investigators will attempt to identify all the major uncertainty contributors and make a reasonable estimation. When an uncertainty statement is required, as discussed previously in Section 2.1, the uncertainty statement will be prepared taking into consideration the instrument uncertainty, calibration standard uncertainty, the data quality objectives and any other applicable factors.

The quantitative uncertainty of a field measurement is not synonymous with the procedural control limits of the instrument. The quantitative uncertainty of a measurement should always be less than the control limits of the measurement procedure. Control limits are established to determine if a field instrument needs to be recalibrated or if data is of sufficient quality to be utilized for decision making purposes. For more information on the control limits used for SESD field measurements, reference the specific SESD field measurement operating procedures.

2.5 Uncertainty Types

The GUM and NIST documents discuss the evaluation of uncertainty according to a “Type A” or “Type B” method of evaluation. The Type A method evaluates standard uncertainty by the statistical analysis of a series of repeated observations. The Type B method evaluates uncertainty based on scientific judgment using all of the relevant information available, which may include:

- previous measurement data
- experience with or general knowledge of the behavior and properties of relevant materials and instruments
- manufacturer’s specifications
- data provided in calibration certificates and other certificates.

Broadly speaking, Type B uncertainty is either obtained from an outside source, or obtained from an assumed distribution based on judgment using all information available.

3 Implementation

3.1 General

Environmental field measurements pose unique challenges for estimating measurement uncertainty. Unlike conducting a Type A uncertainty analysis in a laboratory setting, many times during field measurement activities it is impossible to perform replicate analyses. Supplying a known spike and attempting to determine percent recoveries for many field measurements is also often not possible. Qualitative uncertainty factors as cited in Section 2.2, such as sample handling and constantly changing environmental conditions (temperature as one example), complicate and at times directly impede the ability to conduct a Type A uncertainty estimation of the environment measurements performed in the field. These qualitative uncertainty contributors make a Type A uncertainty estimation of the instruments response to the environmental sample problematic. SESD's routine methodology for estimating its field measurement uncertainty will use a Type B assessment. SESD's implementation of this Type B uncertainty estimation is described in Section 3.2 of this procedure. Uncertainty associated with SESD's field measurements are assumed to be produced from random effects and will be treated as residing in a normal distribution.

In rare circumstances the Type B uncertainty estimation cited in Section 3.2 may not be sufficient for documenting the field measurement uncertainty. For field investigations performed under these circumstances, either a hybrid Type A/B uncertainty (See Section 3.3) or a Type A uncertainty (See Section 3.4) estimation of the field instrument's response to the actual environmental sample would be required. In such a case, the uncertainty evaluation will be interpreted in the context of a thorough understanding of the measurement methodology. For example, in large Category 1 projects with many mobile laboratory field measurements, statistical measures might be undertaken to define the uncertainty of the measurements. Even then, the statistical tests would only be reported in conjunction with the following important elements:

- Previous measurement data,
- Experience with, or general knowledge of, the behavior and property of relevant materials and instruments,
- Manufacturer's specifications,
- Data provided in calibration and other reports, and
- Uncertainties assigned to reference data taken from handbooks.

If it is determined that a hybrid Type A/B uncertainty estimation is needed for the measurements performed during a field investigation, the Type A/B hybrid uncertainty estimation will be computed using Equations 1 through 5 of this procedure. The Type A

portion of this hybrid uncertainty estimation will be computed based on the instrument's response to known standards and not to the instrument's response to the environmental sample itself. Typically, a Type A uncertainty estimation would evaluate the variability of the instrument's response to the environmental sample and not the variability of the instrument's response to a known calibration standard. This is because the performance of an instrument against a known calibration standard will often be more precise than against an environmental sample. However, by combining a Type A uncertainty estimation based on a field instrument performance against known calibration standards along with a Type B estimation of the environmental sample, a total field measurement uncertainty can be estimated. For more detail on the methodology for the SESD hybrid field measurement uncertainty estimation refer to Section 3.3 of this procedure.

If it is determined that a Type A uncertainty estimation is needed for the field measurements performed during an environmental investigation, the uncertainty estimation will be computed using the instruments response to the environmental sample itself and will not be based on a response to calibration standards. For more detail on Type A uncertainty estimations computed solely on the measurements of the environmental sample refer to Section 3.4 of this procedure.

It should be determined during the project planning phase which uncertainty methodology best meets the Data Quality Objectives (DQO)s of the environmental investigation. Using either the hybrid uncertainty estimation or the Type A uncertainty estimation requires that this decision be made prior to field measurements being performed. As such, if it is determined that the uncertainty estimation of the field measurements will use either the hybrid or Type A methodologies, this must be stated in the QAPP and approved by SESD management.

3.2 Routine SESD Uncertainty Estimation for Field Measurements

Through a review of the logbooks of historical environmental sampling activities, manufacturer's instruction manuals and the best professional judgment of the Subject Matter Experts (SME)s for their respective field instruments, the SESD Table of Field Measurement Uncertainties (Type B), SESDFORM-034 (most recent version) has been developed to estimate the Type B uncertainty associated with each type of accredited field instrument utilized by SESD. The uncertainty values found in this table will be used as the field instrument uncertainty for field measurements performed by SESD. The SESD Table of Field Measurement Uncertainties (Type B) will be maintained on the SESD local area network (LAN).

3.3 Hybrid Type A / B Uncertainty Methodology

If it is determined that SESD's routine estimation of field measurement uncertainty is not sufficient for the project's DQOs, the field measurement uncertainty can be determined using a hybrid of both Type A and Type B methodology. The Type B portion of this hybrid methodology is intended to account for the uncertainty associated with the environmental sample. The Type A portion of the hybrid uncertainty assessment will be limited to evaluating the instrument performance against known and traceable calibration standards. The Type A portion of this hybrid uncertainty methodology is only intended to determine instrument variability with respect to known and traceable calibration standards. As such, the instrument response will be compared to the traceable calibration standards and not the environmental sample itself. If the DQOs of an environmental investigation require that the field measurement uncertainty be solely determined by comparing the instrument's response to the environmental sample itself, field investigators will follow Section 3.4 of this procedure.

The assessment of uncertainty through this hybrid methodology will start with a field instrument's operating manual and the quoted uncertainties obtained from a calibration standard's certificate. In addition to the daily calibrations being performed in accordance with the instrument's operating manual, project leaders will perform a post-operation instrument verification check (aka unadjusted calibrations). This verification check will be performed using the appropriate standards at the end of the day or after all measurements have been completed for a particular period of operation. These measurements must be recorded in the field logbook as required per SESDPROC-010 (most recent version).

Type A uncertainty statistics will be computed for each instrument's performance based on these verification checks. At a minimum, the summary statistics will include mean instrument performance as defined by Equation 1, bounded by 95% confidence limits of the mean defined by Equation 4. The "Hybrid" Uncertainty will be computed as the sum of the Type A uncertainty (computed through verification checks), the Type B uncertainty found from SESDFORM-034 (most recent version) and the uncertainty associated with the calibration standards. Equation 5 will be used to compute the estimated hybrid uncertainty. These instrument uncertainties will only be calculated and reported for field measurement equipment that is subject to the scope of field accreditation. Type B uncertainty estimation is used in Equation 5 to compute the hybrid uncertainty estimation, therefore the hybrid uncertainty estimation will always be greater than the Type B uncertainty estimation. This difference can be minimized through the use of accurate calibration standards and obtaining good agreement on the instrument verification checks, but the hybrid uncertainty estimation will always be greater than the Type B uncertainty estimation found from SESDFORM-034 (most recent version).

In some cases, measurement uncertainties are provided in percent as opposed to standard deviations. For these cases, equation 6 will be used to convert all uncertainties into standard deviations so that they may be used in equation 5.

Summary statistics computed for the field instrument's performance against known traceable calibration standards will be computed using the equations in this section of the operating procedure; where Equation 1 is the mean of the verification checks, Equation 2 is the sample standard deviation, Equation 3 is the standard deviation of the mean (aka standard error) and Equation 4 is the 95% confidence limits for the standard deviation of the mean. Because uncertainty is a function of the number of field verification checks, it is not appropriate to compute the field measurement uncertainty using equations 1 through 5 for environmental field investigations that have a small number of instrument verification checks. For this reason, project leaders should endeavor to obtain 7 or more instrument verification checks for a particular measurement type if the below equations are intended to be used to estimate the field measurement uncertainty.

$$\bar{x} = \frac{1}{N} \sum_{i=1}^N x_i$$

Equation 1: Mean

where x_i is the measured verification check, N is the total number of field verification checks, and \bar{x} is the mean of the verification checks

$$s = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N - 1}}$$

Equation 2: Sample Standard Deviation

where x_i is the measured verification check, N is the total number of field verification checks, \bar{x} is the mean of the verification checks, and s is the sample standard deviation

$$\sigma_a = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N(N - 1)}} = \frac{s}{\sqrt{N}}$$

Equation 3: Standard Deviation of the Mean

where x_i is the measured verification check, N is the total number of field verification checks, and \bar{x} is the mean of the verification checks, s is the sample standard deviation, and σ_a is the standard deviation of the verification check mean (\bar{x})

$$\bar{X}_{\pm 95\%} = \bar{x} \pm t_{0.95, n-1} \cdot \sigma_a$$

Equation 4: 95% Confidence Limits of Sample Mean

where \bar{x} is the mean of the verification checks, σ_a is the standard deviation of this mean, $t_{0.95, n-1}$ is the 95th quantile of a t-distribution with n-1 degrees of freedom, and $\bar{X}_{\pm 95\%}$ is the 95% confidence range of the mean verification checks

$$\sigma_{hybrid} = \sqrt{\sigma_a^2 + \sigma_b^2 + \sigma_c^2}$$

Equation 5: Hybrid Uncertainty Estimation

where σ_a is the type a uncertainty found through the standard deviation of this mean verification checks (Equation 3), σ_b is the type b uncertainty for the field instrument of interest (found in SESDFORM-034, most recent version), σ_c is the uncertainty associated with the calibration standards, and σ_{hybrid} is the estimated hybrid uncertainty

$$RSD_x \equiv \frac{\sigma_x}{\bar{x}} * 100$$

Equation 6: Relative Standard Deviation

where σ_x is the standard deviation of the mean, \bar{x} is the value of interest (mean), and RSD_x is the relative standard deviation (uncertainty) expressed as a percent

3.4 Environmental Type A Uncertainty Methodology

When the DQOs of an environmental field investigation require that the Type A uncertainty determination be computed solely on the environmental sample and not based on instruments' agreement to known calibration standards or utilizing a Type B uncertainty estimation, in addition to performing the required verification checks against the

appropriate known standards, SESD field investigators will perform multiple measurements of the environmental sample in question. A minimum of 7 repeat measurements per environmental sample will be performed to allow for a statistically sound sample size. Means of the instrument response to the environmental sample and their associated 95% confidence intervals will be computed. Means will be computed using Equation 1 of this procedure and the 95% confidence interval of this mean will be computed using Equation 4 of this procedure.