Designation: E 2165 – 01

Standard Practice for Establishing an Uncertainty Budget for the Chemical Analysis of Metals, Ores, and Related Materials[1]

This standard is issued under the fixed designation E 2165; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice describes a model for establishing ISO 17025-compliant uncertainty budgets for the chemical analysis of metals, ores, and related materials. It is based on applying the Horwitz[2] function to widely accepted, diverse interlaboratory test programs, such as interlaboratory testing of standard test methods and proficiency testing programs. This function expresses the interlaboratory standard deviations that can be expected for any concentration level as competent laboratories use optimized test procedures to analyze any matrix for any analyte. It may be used to set aim uncertainties against which to plan new standard test methods and to assess the performance of existing test methods.

1.2 An optimized test procedure is one in which the final test results are at least equivalent to alternative, state-of-the-art procedures. In the analytical chemistry community, this means that calibrations are carried out, verified, and controlled such that the final test results have no systematic, detectable bias. The elimination of sources of bias is a key responsibility of any person who designs analytical test methods. Hence, an analytical test method that contains systematic, measurable sources of bias would probably not be accepted as an ASTM test method and its performance data would probably not be in compliance with the procedures described in this practice.

1.3 The uncertainty budget model described in this practice is based on the assumption that, in a normally distributed, bias-free environment, measurement uncertainty will improve by the square root of two with each removal of a significant source of variation. Conversely, it is assumed that measurement uncertainty will worsen by the same amount with each addition of a significant source of variation. Furthermore, this model assumes that the hierarchy of increasing variation in any composition-based measurement system begins with calibration and progresses through control to intralaboratory standard deviation to interlaboratory standard deviation to product sampling for conformity assessment. Therefore, aim values for the expected uncertainties at any process step can be predicted using this model.

1.4 When using this model, the aim values generated using this model must then be validated, verified, and documented as part of the development and interlaboratory testing of any new test method, sampling practice, and product specification, as appropriate. It is also expected that each laboratory that elects to use that standard test method will generate data to show that the standard test method complies with the published uncertainties developed during interlaboratory testing of the standard test method. The principles in this practice can also be applied to the development of test methods used to determine the composition of other materials.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores and Related Materials[3]

E 1282 Guide for Specifying the Chemical Compositions and Selecting Sampling Practices and Quantitative Analysis Methods for Metals, Ores, and Related Materials[3]

E 1329 Practice for Verification and Use of Control Charts in Spectrochemical Analysis[3]

E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method[3]

E 2027 Practice for Conducting Proficiency Tests in the Chemical Analysis of Metals, Ores, and Related Materials[4]

E 2053 Guide for Planning, Carrying Out, and Reporting Traceable Chemical Analyses of Metals, Ores, and Related Materials[4]

E 2093 Guide for Optimizing, Controlling and Reporting Test Method Uncertainties from Multiple Workstations in the Same Laboratory Organization[4]

2.2 *ISO Standards:*

[1] This practice is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.22 on Statistics and Quality Control.

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[2] Horwitz, W., *Analytical Chemistry*, Vol 54, pp. 67A-76A, 1982.

[3] *Annual Book of ASTM Standards*, Vol 03.05.

[4] *Annual Book of ASTM Standards*, Vol 03.06.

ISO 17025 (1999) General Requirements for the Competence of Calibration and Testing Laboratories[5]

ISO 9000: 2000 Quality Management and Quality System Elements[5]

ISO/TS 16949 (2002) Quality Systems—Automotive Suppliers—Particular Requirements for the Application of ISO 9001:1994[5]

ISO TC/17 SC 1 Steel—Methods and Determination of Chemical Composition[5]

2.3 *Other Document:*

QS9000, 3rd Edition Quality System Requirements, Chrysler Corporation, Ford Motor Company, and General Motors Corporation[6]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this guide, refer to Terminology E 135.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *aim calibration uncertainty*—the maximum deviation (95 % confidence) to be allowed between an assumed true value and the measured value during the design of the calibration segment of an analytical test method, based on an aim uncertainty budget. In order to ensure that the calibration function does not contribute distinguishable bias to the report value, all individual calibration deviations shall be randomly distributed above and below the assumed true value. It is the method-developer's responsibility to develop and test appropriate protocols for detecting and controlling calibration bias consistent with the intended purpose of the test method and the measuring technology being utilized.

3.2.2 *aim control uncertainty*—the maximum deviation (95 % confidence) to be allowed in the design of the control part of an analytical test method, based on an aim uncertainty budget and including variation due to calibration. Since most control charts are created with three sigma control limits, users must design and control measurement processes to be effective at the 95 % confidence level. To help meet this requirement, it is recommended that control charts used in this model be interpreted using the Westgard rules in accordance with Practice E 1329.

3.2.3 *aim total intralaboratory uncertainty*—the maximum deviation (95 % confidence) to be allowed in the design of the total intralaboratory uncertainty of a test method, beginning with the preparation of a homogeneous sample and ending with a final report value to the client.

3.2.4 *aim total interlaboratory uncertainty*—the maximum deviation (95 % confidence) to be allowed in interlaboratory studies of a test method, based on multipurpose interlaboratory studies of the type carried out in proficiency tests and national and international standard test development studies.

3.2.5 *aim lot uncertainty*—the maximum deviation (95 % confidence) to be allowed when optimized, standardized sampling practices are used to take samples from a specified lot of material and the samples are distributed among several competent laboratories for testing.

3.2.6 *uncertainty budget*—the allocation of total measurement uncertainty among specific components of a measurement process that contribute significantly to the overall deviation.

4. Significance and Use

4.1 Knowing and controlling the uncertainty of measurements are important to laboratories as they comply with internal and external needs. For example:

4.1.1 There is a need to know when calibration curves drift so that corrections can be made before time is wasted generating faulty data and, more importantly, to prevent reporting of faulty data. The control of laboratory performance against internally established criteria is usually met with good statistical control programs, such as described in Practice E 1329.

4.1.2 There is a need to demonstrate state-of-the-art performance to customers and accreditation bodies, especially those accrediting laboratories to ISO 17025. One widely accepted way to demonstrate compliance is to participate in proficiency test programs, such as described in Practice E 2027, as available.

4.1.3 There is a need for laboratory management personnel to know, in advance, how tightly to control existing processes, how to set data quality expectations for new work, and how to build uncertainty statements and budgets to comply with ISO 17025. This practice gives one approach for meeting those needs.

4.1.4 There is a need for users of test results to understand the origin of measurement uncertainties and how to apply them in using data for process control or product conformity decisions in order to comply with ISO 9000, ISO/TS 16949, and QS 9000. This practice gives a relatively simple model for use in developing strategies to meet those needs, utilizing the information available from the analytical testing laboratory.

4.2 ISO 17025 accepts laboratory compliance with uncertainty budgets in standard test methods, provided that all of the significant sources of variation are identified and quantified in the standard test method. This practice offers a consensus-based approach to meeting that need, based on the most widely available sources of comparative data available, namely interlaboratory standard deviations.

4.3 Building the model used in this practice on the available interlaboratory standard deviations is convenient because they are in the "middle" of the steps between calibration and final data usage and are at the interface between the laboratories and their clients. Hence, any inaccuracies in the model, either in the laboratory or in the user environment, will be correctable within either community without disturbing the foundation of the model.

4.4 Having allowed for the fact that this model is based on probabilities at the 95 % confidence level, any task group that considers promulgating a standard test method, practice, or specification that exceeds the boundaries set by this practice should seek opportunities to improve the procedure or be prepared to accept uncertainties that exceed normally accepted levels.

4.5 This model is based on 95 % confidence intervals (two

[5] Available from American National Standards Institute, 25 W. 43rd St., 4th Floor, New York, NY 10036.

[6] Available from Automotive Industry Action Group (AIAG), 26200 Lahser Rd., Southfield, MI 48034.

standard deviations). Users must be aware that, at 95 % confidence, one in twenty values will fall outside of the aim. In order to maintain fewer "outliers," users should try to operate just below the "maximum" values listed in this practice.

4.6 Users must be aware that, in order to compare the results from two laboratories that perform the same experiment on the same material, the maximum variation to be expected between those laboratories is calculated by multiplying the aim variation by the square root of two.

4.7 It is anticipated that those who write and test standard test methods will use this practice to establish aim uncertainty budgets for use during test method development, validation, and interlaboratory testing. Test methods that are capable of performing at or better than the calibration, control, total intralaboratory, and interlaboratory uncertainties described in this practice should be considered state of the art when carried out by competent (ISO 17025 compliant) laboratories and can be expected to meet all reasonable commercial and proficiency test requirements.

4.8 It is anticipated that those who write and test in-house methods will use this practice to establish local aim uncertainty budgets for use during test method development, validation, and intralaboratory testing. Test methods that are capable of performing at or better than the calibration, control, and total intralaboratory uncertainties described in this practice should be considered state of the art when carried out by competent (ISO 17025 compliant) laboratories. They can be expected to meet all reasonable commercial and proficiency test requirements, and should be viable candidates for subsequent evaluation and promulgation as standard test methods.

5. Procedure

5.1 Locate a large database of interlaboratory standard deviations that were developed using state-of-the-art techniques and that best represent the type of test methods to which the model will be applied. Construct a log-log plot of interlaboratory standard deviations (95 % confidence) versus concentration without regard to matrix, analyte, or test method. Perform a power-fit to create a linear equation that best describes the relationship. Two examples are as follows:

5.1.1 Interlaboratory test data from ISO TC/17 SC 1 fit to the Horwitz[2] function, is shown in the annex of Guide E 2093. The interlaboratory standard deviation (95 % confidence) (R2/sqrt(2)) is shown in Eq 1 as follows:

$$y = 0.0303x^{0.6661} \quad (1)$$

where:

y = 2 times interlaboratory standard deviation, i.e., 2 sigma, 95 % confidence, and

x = analyte concentration, m/m, %.

5.1.2 Interlaboratory test data from 2 years (1999-2000) of ASTM's Proficiency Test Programs for Plain Carbon Low Alloy Steel and Stainless Steel is shown as Eq 2:[7]

$$y = 0.0384x^{0.58} \quad (2)$$

where:

y = 2 times interlaboratory standard deviation, i.e., 2 sigma, 95 % confidence, and

x = analyte concentration, m/m, %.

Since both of these plots predict very similar standard deviations, either can be used to establish anticipated interlaboratory standard deviations for metals and related materials. For purposes of this practice, the option in 5.1.1 is used in this practice.

5.2 Construct a data table along the lines illustrated in Table 1 (Notes 1 and 2).

NOTE 1—If the ISO data described in 5.1.1 is suitable for the intended purpose, then Table 1 can be used.

NOTE 2—Table 1 includes more digits past the decimal point than would be used in a typical uncertainty budget. They are included here to help the reader understand the level of variation to be expected at different concentration ranges. The data in the table is calculated from the interlaboratory standard deviations (95 % confidence) as described as follows. The data illustrates the magnitude of the uncertainty budget components at selected concentrations.

5.2.1 Select a series of analyte concentrations of interest and list them in increasing order in the column labeled "Concentration, %(m/m)." These selections might represent evenly distributed values across the concentration ranges of interest, or high, middle, and low values from specification or method scopes.

5.2.2 Enter a series of headings as follows: "Intralaboratory Calibration," "Intralaboratory Control," "Intralaboratory Total," "Interlaboratory Total," and, "Interlaboratory Lot."

5.2.3 Under "Total Interlaboratory," enter the interlaboratory (95 % confidence) precision calculated from the log-log relationship for each concentration selected for evaluation. This is the actual test data from which all other estimates within the model are calculated.

5.2.4 Under "Total Intralaboratory," enter the interlaboratory value (5.2.3) divided by the square root of two for each

TABLE 1 Example Aim Uncertainty Budget Calculations (Based on ISO TC 17/SC 1, 5.1.a)

	Intralaboratory			Interlaboratory	
Concentration, %, mm	Calibration[A]	Control[B]	Total[C]	Total[D]	Lot[E]
0.001	0.00011	0.00015	0.00022	0.00030	0.00043
0.005	0.00032	0.00045	0.00063	0.00089	0.00126
0.010	0.00050	0.00071	0.00100	0.00141	0.00280
0.015	0.00065	0.00093	0.00131	0.00185	0.00260
0.050	0.00147	0.00207	0.00292	0.00412	1.00581
0.100	0.00233	0.00329	0.00464	0.00654	0.00922
0.50	0.00681	0.00960	0.01354	0.01910	0.02692
1.00	0.01081	0.01524	0.02149	0.03030	0.04272
5.00	0.03158	0.04452	0.06278	0.08852	0.12481
10.0	0.05011	0.07065	0.09961	0.14046	0.19804
20.0	0.07951	0.11210	0.15807	0.22287	0.31425
30.0	0.10416	0.14686	0.20708	0.29198	0.41169
40.0	0.12616	0.17788	0.25082	0.35365	0.49865
50.0	0.14638	0.20639	0.29101	0.41032	0.57856
60.0	0.16528	0.23304	0.32859	0.46331	0.65326
70.0	0.18315	0.25824	0.36412	0.51341	0.72390
80.0	0.20019	0.28226	0.39799	0.56117	0.79124
90.0	0.21652	0.30530	0.43047	0.60696	0.85582

[A] See 3.2.1.
[B] See 3.2.2.
[C] See 3.2.3.
[D] See 3.2.4.
[E] See 3.2.5.

[7] Flinchbaugh, D.A., Crawford, L.F., and Bradley, D. Accred. Qual Assur (2001), pp 493–500.

concentration. This represents the maximum uncertainty a single laboratory can have and still comply with the "Interlaboratory Total" Uncertainty requirement.

5.2.5 Under "Control," enter the Intralaboratory value (5.2.4) divided by the square root of two for each concentration. This represents the maximum uncertainty (95% confidence) a single laboratory can have on a control standard and still comply with the "Intralaboratory Total" Uncertainty requirement (Note 3).

NOTE 3—Since most control charts are based on 3-sigma control limits, care must be taken in establishing within-laboratory control practices to ensure compliance with the model. For example, since this model is based on 95 % confidence, a laboratory that uses 3-sigma control limits must ensure that its 3-sigma control limits are no more than 1.5 times the value predicted in the control column.

5.2.6 Under "Calibration," enter the "control" value divided by the square root of two for each concentration. This represents the maximum uncertainty a single laboratory can have in its calibration function and still comply with the "interlaboratory total" uncertainty requirement (Note 4).

NOTE 4—If a laboratory's control statistics are considerably better than the maximum allowed in 5.2.5, then it is mathematically possible for that laboratory to exceed the calibration limit by a small amount and still comply with the 5.2.4 expectation. However, this is not recommended, particularly since this model is based on 95% confidence.

5.2.7 Under "lot," enter the "interlaboratory total" value multiplied by the square root of 2 for each concentration. This represents the maximum uncertainty a user should expect when a lot of material is sampled for analysis for conformity assessment (Note 5).

NOTE 5—It must be recognized that, unlike the intralaboratory and interlaboratory components, there is not much data to support the amount of variation due to sampling.

6. Implementation

6.1 This model predicts the expected uncertainty in state-of-the-art facilities where all sampling and analysis procedures are known to be bias-free and carried out by competent (ISO 17025 compliant) organizations, and test materials are known to be homogeneous. Predictability of attainability of a specified performance level does not guarantee compliance. Compliance must be validated, verified, and documented.

6.2 Those who write product specifications, in accordance with Guide E 1282, can use this practice to predict the expected measurement uncertainty when the material compositions being specified are subject to conformity assessment by sampling and analysis by multiple facilities using optimized state-of-the-art protocols. If the test data variability predicted by the model in this practice is too great to allow practical assessments, then consideration should be given to redefining the specification in a way that allows meaningful testing.

6.3 Those who write standard test methods can use this practice to predict the expected measurement uncertainty when the test method is evaluated in an interlaboratory test, such as by following Practice E 1601. In order to claim that the test method is bias-free, it is recommended that the task group apply the principles of Guide E 2053, as appropriate. By designing test methods and demonstrating that they are capable of complying with the uncertainty budget model in Guide E 2053, confidence is increased that the final interlaboratory test data will be satisfactory.

6.4 Those who write in-house test methods based on standard test methods can use this practice and the standard test method to create their own local standard operating procedure and uncertainty budget. If full compliance with the standard test method is intended, then the laboratory's uncertainty budget statements need only show data demonstrating compliance with the uncertainty budget in the standard test method. Laboratories that use multiple workstations to perform the same standard test method should refer to Guide E 2093 for guidance on how to coordinate all workstations efficiently.

6.5 Those who write in-house test methods that are not based on standard test methods, but are envisioned to become standard test methods or are to be compliant with ISO 17025 should follow all of the procedures in this practice, including building an uncertainty budget for calibration, control, and total intralaboratory variation as shown in Table 1.

6.6 Those who write standard sampling practices can use this practice to predict the measurement variation to be expected when test methods developed in compliance with 6.2 are used to evaluate those samplers and sampling practices. When using this model to evaluate sampling practices in an interlaboratory test mode, the maximum errors should comply with the "Interlaboratory Lot" column in Table 1.

6.7 Those who study the optimization of industrial processes or wish to make conformity assessment decisions can use the "Lot" column in Table 1 as an indicator of the combined sampling and measurement errors they can expect in an optimized environment. Comparing that information with available process control and final shipment test data can indicate the potential for improving the present sampling and analysis systems and the relative benefits to be achieved by making those improvements.

7. Keywords

7.1 practice; uncertainty budget; uncertainty statement