INTERNATIONAL

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Standard Practice for Within-laboratory Quantitation Estimation (WQE)[1]

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1. Scope

1.1 This practice establishes a uniform standard for computing the within-laboratory quantitation estimate associated with *Z* % relative standard deviation (referred to herein as $WQE_{Z\,\%}$), and provides guidance concerning the appropriate use and application.

1.2 $WQE_{Z\,\%}$ is computed to be the lowest concentration for which a single measurement from the laboratory will have an estimated *Z* % relative standard deviation (*Z* % RSD, based on within-laboratory standard deviation), where *Z* is typically an integer multiple of 10, such as 10, 20, or 30. *Z* can be less than 10 but not more than 30. The $WQE_{10\,\%}$ is consistent with the quantitation approaches of Currie (**1**)[2] and Oppenheimer, et al. (**2**).

1.3 The fundamental assumption of the WQE is that the media tested, the concentrations tested, and the protocol followed in developing the study data provide a representative and fair evaluation of the scope and applicability of the test method, as written. Properly applied, the WQE procedure ensures that the WQE value has the following properties:

1.3.1 *Routinely Achievable WQE Value*—The laboratory should be able to attain the WQE in routine analyses, using the laboratory's standard measurement system(s), at reasonable cost. This property is needed for a quantitation limit to be feasible in practical situations. Representative data must be used in the calculation of the WQE.

1.3.2 *Accounting for Routine Sources of Error*—The WQE should realistically include sources of bias and variation that are common to the measurement process and the measured materials. These sources include, but are not limited to intrinsic instrument noise, some typical amount of carryover error, bottling, preservation, sample handling and storage, analysts, sample preparation, instruments, and matrix.

1.3.3 *Avoidable Sources of Error Excluded*—The WQE should realistically exclude avoidable sources of bias and variation (that is, those sources that can reasonably be avoided in routine sample measurements). Avoidable sources include, but are not limited to, modifications to the sample, modifications to the measurement procedure, modifications to the measurement equipment of the validated method, and gross and easily discernible transcription errors (provided there is a way to detect and either correct or eliminate these errors in routine processing of samples).

1.4 The WQE applies to measurement methods for which instrument calibration error is minor relative to other sources, because this practice does not model or account for instrument calibration error, as is true of most quantitation estimates in general. Therefore, the WQE procedure is appropriate when the dominant source of variation is not instrument calibration, but is perhaps one or more of the following:

1.4.1 *Sample Preparation,* and especially when calibration standards do not go through sample preparation.

1.4.2 *Differences in Analysts,* and especially when analysts have little opportunity to affect instrument calibration results (as is the case with automated calibration).

1.4.3 *Differences in Instruments (measurement equipment),* such as differences in manufacturer, model, hardware, electronics, sampling rate, chemical-processing rate, integration time, software algorithms, internal signal processing and thresholds, effective sample volume, and contamination level.

1.5 *Data Quality Objectives*—For a given method, one typically would compute the WQE for the lowest RSD for which the data set produces a reliable estimate. Thus, if possible, $WQE_{10\,\%}$ would be computed. If the data indicated that the method was too noisy, so that $WQE_{10\,\%}$ could not be computed reliably, one might have to compute instead $WQE_{20\,\%}$, or possibly $WQE_{30\,\%}$. In any case, a WQE with a higher RSD level (such as $WQE_{50\,\%}$) would not be considered, though a WQE with RSD < 10 % (such as $WQE_{5\,\%}$) could be acceptable. The appropriate level of RSD is based on the data quality objective(s) for a particular use or uses. This practice allows for calculation of WQEs with user selected RSDs less than 30 %.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the*

[1] This practice is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.02 on Quality Systems, Specification, and Statistics.

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[2] The boldface numbers in parentheses refer to the list of references at the end of this standard.

Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 *ASTM Standards:*[3]
D1129 Terminology Relating to Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
E2586 Practice for Calculating and Using Basic Statistics

2.2 *BIPM Documents:*
GUM: JCGM 100:2008 Evaluation of measurement data—Guide to the expression of uncertainty in measurement[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology D1129, Practice E2586, and the GUM.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *censored measurement, n*—a measurement that is not reported numerically, but is stated as a "nondetection" or a less-than (for example, "less than 0.1 ppb").

3.2.2 *quantitation limit (QL) or limit of quantitation (LQ), n*—a numerical value, expressed in physical units or proportion, intended to represent the lowest level of quantitation, based on a set of criteria for quantitation.

3.2.2.1 *Discussion*—The WQE is an example of a QL.

3.2.3 *Z % within-laboratory quantitation estimate ($WQE_{Z\,\%}$), n*—(in accordance with Currie (**1**))—The lowest concentration for which a single measurement from the examined laboratory will have an estimated *Z* % relative standard deviation (*Z* % RSD, based on the within-laboratory standard deviation).

4. Summary of Practices

4.1 The WQE procedure provides an estimate of the true concentration at which a desired relative precision is achieved. Whether from analysis of routine quality samples or from studies undertaken from time to time (or both), the first step is to acquire data representative of the laboratory performance for use in the WQE calculations. Such data must include concentrations suitable for modeling the precision and bias over a range of concentrations. Each datum for a method/matrix/analyte should represent an independent sample where routine sources of measurement variability occur at typical levels of influence. Outlying individual measurements should be eliminated, using an accepted, scientifically-based procedure for outlier identification and a documented, scientific basis for removal of data from the data set, such as found in Practice D2777. WQE computations must be based on retained data (after optional outlier removal) from at least six independent measurements at a minimum of five concentrations.

4.2 Retained data are analyzed to identify and fit one of four proposed standard-deviation models: *constant*, *linear* (straight-line), *hybrid* (proposed by Rocke and Lorenzato (**3**)), and *exponential*. These models describe the relationship between the within-laboratory standard deviation of measurements and the true concentration, *T*. The selection process involves evaluating the models, starting with the linear model and performing statistical tests to choose the simplest model that adequately fits the data. Evaluation includes statistical significance testing and residual analysis, and requires the judgment of a qualified chemist.

4.3 Once the standard-deviation model has been selected, it determines the fitting technique for the model of measured concentration versus true concentration, referred to in this practice as the *mean-recovery model*. If the standard deviation is constant, then ordinary least squares may be used. If the standard deviation is not constant, the predicted standard deviations are used to generate weights for use in weighted least squares. Regardless of the fitting technique, the mean-recovery model fits a straight line to the data.

4.4 The linear regression (measured versus true) is evaluated for statistical significance, for lack of fit, and for residual patterns.

4.5 These two models (standard deviation and recovery) are then used to calculate the WQE values. Either a direct calculation or iterative algorithm (depending on the model) is used to compute $WQE_{10\,\%}$, the lowest true concentration with estimated RSD = 10 % (*Z* = 10); $WQE_{20\,\%}$ (%RSD = 20 = *Z*); and $WQE_{30\,\%}$ (%RSD = 30 = *Z*). If needed for particular data-quality objectives (DQOs), $WQE_{Z\,\%}$ may be computed for some $Z < 10$. The particular *Z* % selected for use should depend upon the data-quality needs and the realized performance. Typically, either 10 % or 20 % is used in environmental water testing. The 30 % RSD approaches the criterion for detection. *Z* values greater than 30 should not be used. An RSD of 5 % approximates a level at which at least one sure significant digit has been achieved.

5. Significance and Use

5.1 Appropriate application of this practice should result in a WQE achievable by the laboratory in applying the tested method/matrix/analyte combination to routine sample analysis. That is, a laboratory should be capable of measuring concentrations greater than $WQE_{Z\,\%}$, with the associated RSD equal to *Z* % or less.

5.2 The WQE values may be used to compare the quantitation capability of different methods for analysis of the same analyte in the same matrix within the same laboratory.

5.3 The WQE procedure should be used to establish the within-laboratory quantitation capability for any application of a method in the laboratory where quantitation is important to data use. The intent of the WQE is not to impose reporting limits. The intent is to provide a reliable procedure for establishing the quantitative characteristics of the method (as

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] Available from https://www.bipm.org/en/publications/guides/, accessed May 2021.