Designation: D7783 – 13

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 the 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 would 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 was 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 quantiation 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 lowest % RSD possible for any given data set. Thus, if possible, $WQE_{10\ \%}$ would be computed. If the data indicated that the method was too noisy, 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 $WQE_{1\ \%}$) would 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] 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 a list of references at the end of this standard.

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

D6091 Practice for 99 %/95 % Interlaboratory Detection Estimate (IDE) for Analytical Methods with Negligible Calibration Error

D6512 Practice for Interlaboratory Quantitation Estimate

D7510 Practice for Performing Detection and Quantitation Estimation and Data Assessment Utilizing DQCALC Software, based on ASTM Practices D6091 and D6512 of Committee D19 on Water

E1763 Guide for Interpretation and Use of Results from Interlaboratory Testing of Chemical Analysis Methods

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology D1129.

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 level of (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. These models describe the relationship between the within-laboratory standard deviation of measurements and the true concentration, T. The identification process involves evaluating the models in order, from simplest to most complex: constant, straight-line, exponential, and hybrid (proposed by Rocke and Lorenzato (**3**) and Guide E1763. Evaluation includes statistical-significance testing and residual analysis, and is based on the best judgment of a qualified chemist and the requirement to utilize the simplest model that adequately fits the data.

4.3 Once the standard-deviation model has been determined, it is used to determine the fitting technique for modeling measured concentration (referred to in this practice as the mean-recovery model) to true concentration. If standard deviation is constant, then ordinary least squares is used. If standard deviation is not constant, the modeled standard-deviation predictions are used to generate weights for use in the weighted-least-squares fitting. With either fitting technique, a straight line is the model that is fitted to the data.

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

4.5 These two models (standard-deviation and calibration) are then used to calculate the WQE values. Either a direct or interactive 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 implemented in the laboratory for the matrix and analyte) and thus to provide the laboratory with reliable information characterizing the uncertainty in any data produced. Then the

[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.

laboratory may make informed decisions about censoring data and has the information necessary for providing reliable estimates of uncertainty with reported data.

6. Procedure

6.1 This procedure is described in stages as follows: Development of Data, Data Screening, Modeling Standard Deviation, Fitting the Recovery Relationship, and Computing the Quantitation Estimates.

6.2 *Development of Data for Input to the Calculations*—A single WQE calculation is performed per analyte, matrix/medium and method. A minimum of five concentrations must be used to allow for high-quality estimation of true-verses-measured concentration, and for modeling the relationship of standard deviation to true concentration. A minimum of six values at each concentration are required to provide a high-quality estimation of the standard-deviation and the recovery relationships. Additional concentrations (especially additional, representative, independent samples at each concentration) are highly encouraged; such inclusion will reduce the uncertainty in the estimate and better assure that after outlier removal, the minimum requirements for concentrations and values will be met. Data for each WQE calculation should come from only one laboratory, one method, and be for only one analyte in one matrix/medium. Concentrations may be designed in advance or data already developed may be used. For multi-laboratory determinations, see Practice D6091.

6.2.1 *Designing Concentrations*—Where concentrations are being selected in advance of the collection of data, the development of an optimized design should consider many factors, including:

6.2.1.1 Concentrations of available data, such as routine quality-control samples.

6.2.1.2 Potential use of the same data to calculate detection limits and or other control limits.

6.2.1.3 The anticipated or previously determined WQE (study range should exceed this value by at least a factor of 2).

6.2.1.4 The potential need to eliminate the lowest concentration(s) selected (see zero-concentration discussion above).

6.2.1.5 Where possible, select a WQE study design that has enough distinct concentrations to assess statistical lack of fit of the models (see Draper and Smith (**4**)). Recommended designs are: (*a*) The semi-geometric design with five or more true concentrations, T_1, T_2, and so forth, such as: 0, WQE_0/D^2, WQE_0/D, WQE_0, $D \times WQE_0$, $D^2 \times WQE_0$, where D is a number greater or equal to 2 and WQE_0 is an initial estimate of the WQE, (*b*) equi-spaced design: 0, $WQE_0/2$, WQE_0, $(3/2) \times WQE_0$, $2 \times WQE_0$, $(5/2) \times WQE_0$. Other designs with at least five concentrations—provided the design includes blanks, one concentration approximates $2 \times WQE_0$, and at least one nonzero concentration below WQE_0—should be adequate.

6.2.2 *Considerations for All Concentration Selections:*

6.2.2.1 The range of the data, the number of unique concentrations, and the spacing of the concentration are the primary decisions for study design, in addition to the number of replicates at each concentration. The range chosen, excluding the zero value for purposes of the discussion of range, should be from below the estimated detection level to above the WQE of interest (for example, 10 %, 20 %, or 30 %), so as to allow for performance of calculations without the need for extrapolation.

6.2.2.2 A single model (one of the four models in this practice) should describe the behavior of the standard deviation in this range. The anticipated form of the relationship between measurement standard deviation and true concentration, if known, can help in choosing design spacing. Chemistry, physics, empirical evidence, or informed judgment may make one model more likely than others. Evaluation of interlaboratory method-validation studies may also provide information about these relationships. If a model of standard deviation is likely to be one with curvature at lower concentrations (hybrid or exponential) then a semi-geometric design is favored. If the likely relationship is constant or straight-line, then equidistant spacing might be favored.

6.2.2.3 Additional concentrations, beyond the minimum of five concentrations, is strongly recommended where knowledge of these relationships is unknown. Where more than one order of magnitude is covered in the range selected (per range definition in 6.2.2.1), it is recommended that four additional unique concentrations be added per additional order of magnitude greater than one.

(1) Where ongoing quality-control (QC) information is available and it indicates that precision is good at the concentration of this quality control measure, (for example, 5 % RSD or less, at higher concentrations), then establishing the maximum concentration for the study at or below that concentration should be considered where the % RSD criterion for the WQE is higher (for example, a WQE 10 %).

(2) Where ongoing QC demonstrates a high % RSD (for example, above 30 %), several concentrations at and above the concentration of the QC sample should be included.

NOTE 1—Where more than five concentrations are available, determination of the WQE with and without the highest (and potentially the lowest) concentration(s) included can provide insight into the effects of the highest concentration(s) on the recovery relationship and the modeling of standard deviation. Calculation of the WQE values based on the most appropriate and applicable concentrations, so long as minimums are met, is allowed.

6.2.2.4 The minimum of six independent values at each concentration is required by this practice to provide a minimally acceptable data set for calculation of standard deviation at each concentration. Increasing the number of levels is desirable where project constraints allow. It is not required that the same number of replicates be used for each concentration; however, extreme differences (for example orders of magnitude) should be avoided.

6.2.2.5 Known, routine sources of measurement variability, consistent with those of routine analysis of samples, must have been in action at the time of the generation of the data to be used, if the WQE is to be used for characterizing routine performance. That is, in order for the WQE to represent routinely achieved quantitation, the data used for WQE calculation must be generated under routine analytical conditions. Representative within-laboratory variation can only be seen if the number of qualified analysts and qualified measurement systems in the laboratory are represented. The data used and the more combinations included, the less effect any specific

bias in these pairings should have on the WQE estimate. Similarly, sample management (for example, holding time) and allowed variations in routine sample-processing procedures must be included. The time period spanned must allow routine, time-dependent sources of variation to affect the testing. This consideration should include factors such as the frequency of calibration of instruments, introduction of newly prepared or purchased standards, reagents and supplies, and sample-holding times. Historically, the failure to utilize representative data in determination of quantitation limits has been a primary component in over-statements of quality through quantitation-limit values and should be strictly avoided (that is, garbage in, garbage out). Ideally, each measurement would be a double-blind measurement made by a different analyst, using a different (qualified) measurement system on a different day. Optimally, data to be used should be either completely blind, or from known but completely routine, integrated testing (such as routine quality-control data). In any case, the goal is to minimize special treatment of the WQE test samples.

6.2.2.6 Where the WQE is meant to represent the best possible performance, and not routine performance, then optimized conditions for data generation would be appropriate. Similarly, if the performance of only a single process, instrument system, analyst, etc. is of interest, only the applicable variables should be included. It is the responsibility of the user of this practice to assure that the appropriate data are utilized for the end use(s) of WQE. Where the end use is unknown, the data generator who is using the WQE needs to disclose the specific attributes of the data used in the calculation (as well as the % RSD), and thus of the WQE.

6.2.2.7 Where preexisting, routine-source data (for example, quality-control data) are used, care must be taken to assure that: (*1*) each data point represents a true and independent sampling of the population (as well as of the sample medium being examined, where applicable) and (*2*) all sample-processing steps and equipment (for example, bottles, preservatives, holding, preparation, cleanup) are represented. Also, "true" concentration levels must either be known (that is, true "spiked" concentration levels), or knowable, after the fact. A concentration is considered *known* if reference standards can be purchased or constructed, and *knowable* if an accurate determination can be made.

6.2.2.8 Transformation of other types of data (such as laboratory replicates, which under-represent the variability as compared to independent samples and usually do not have known true concentrations), using scientifically and statistically sound approaches is not prohibited by this practice. However, care must be taken and the validity of these transformations tested. It is also critical that any standards used to prepare study samples be completely independent of the standards used to calibrate the instrument.

6.2.2.9 Blank correction should not be performed, unless the method requires this correction to calculate result values.

6.2.3 *True-Concentration Zero (Blank) Data Discussion*—Where possible, it is preferable to include data from samples with true concentration of zero (for example, blanks). However, for many methods, it may not be possible to conduct an unbiased sampling of the zero (blank) concentration samples, since instruments and software systems routinely smooth electronic information (raw data) from the detector and through software settings that censor reported data. Through these automated processes, many testing instruments return to the operator a result value of "zero," when, if these processes had been turned off, a non-zero numeric result (positive or negative) would have been produced. These "false-zero" values adversely affect the use of the zero-concentration data in statistics and should not be used for WQE studies. Most chromatography systems (and many other types of computer-assisted instruments) have instrument set-points (such as (digital) bunch rate, slope sensitivity, and minimum area counts) that are operator-controllable. For purposes of this study, generating as much uncensored low-level data as practical is important and the presence of these processes as well as the setting of any operator-controllable setting should be evaluated.

NOTE 2—Qualitative criteria used by the method to identify and discriminate among analytes are separate criteria, and must be satisfied according to the method.

6.2.3.1 Once true-concentration-zero measurements have been generated, and prior to use, it is important to examine and evaluate these data. A graph of measured concentration by frequency of occurrence may be helpful. However, unless a fairly large sample size is represented (for example, n>20), the distribution may be distorted by the random nature of sampling alone. As a general rule, if there were no bias, then on average and over a large sampling, a truly uncensored set of zero-concentration (blank) data would have a mean of zero with approximately half of the results being negative values and half positive, and be Normally distributed. If some positive or negative bias were present, the percentages would shift. However, in general the frequency should be higher near the mean of the values and should decline as the concentrations move away from the mean, with approximately half of the non-mean data above and half below the mean.

(1) Blank data are considered suspect if: (*1*) there is no variation in these data, (*2*) there are an inordinate number of zero values (and no negative values) relative to the frequencies of positive values (6.2.3 above), (*3*) if there is a high frequency of the lowest value in the data set (for example, where minimum-peak-area rejection has been used) relative to the frequency of higher concentration values, and few or no lower values, or (*4*) a frequency graphic does not begin to approximate a bell curve (when there are 20 or more samples).

(2) If the distribution of the data is suspect, the literature, plus instrument-software and equipment manuals, should be consulted. These documents can provide an understanding of: (*1*) the theory of operation of the detection system, (*2*) the signal processing, calibration, etc., and (*3*) other aspects of the conversion of response to reported values. Judgment will be needed to determine whether to use some or all of the true-concentration-zero (blank) data, or to exclude the data from the calculations. In general, if less than 10 % of the zero-concentration data are: (*1*) censored, (*2*) suspect, or (*3*) false-zeros, then these "problem" data should be removed. Only the remaining blank data are used in the WQE calculations; there must be at least six replicates. Where the zero

concentration is excluded or is not possible to obtain, it is important to include a true concentration as close as possible to zero in the study design.

(3) Where 75 % or less of the data are censored or smoothed, and there are at least six remaining values, it is reasonable to use statistical procedures to simulate the distribution that is missing or smoothed. Software procedures are commercially available. Additionally, procedures such as log-normal transformation may be used to accommodate data that are not normally distributed. The presence of zero-concentration in the study data and in the WQE is not as critical as inclusion of such data in the WDE calculations. Therefore, the decision about inclusion or exclusion of zero-concentration data in a WQE data set should weigh: (*1*) the number of other concentrations available, (*2*) the range of the other concentrations, and (*3*) the risk of extrapolation of the WQE outside the data-set concentration range against the quality of the zero-concentration data.

6.2.3.2 *True Concentrations Near Zero*—As with concentration zero, true concentrations very near to zero may also have been censored, smoothed, and contain false-zeros. Examination of these very low concentrations, as above for zero concentration, is important. The likelihood of occurrence and the percentage of data affected decreases with increasing concentration.

6.3 *Data Screening, Outlier Identification, and Outlier Removal:*

6.3.1 Data that are to be the input to the WQE calculation should be screened for compliance with this practice's conditions, appropriateness for the intended use of the WDE, obvious errors, and individual outliers. Graphing of the data (true versus measured) is recommended as an assistive visual tool. This graphic is available in the DQCALC software.

6.3.2 Outlying individual measurements must be evaluated; if determined to be erroneous, they should be eliminated using scientifically-based reasoning. Identification of potential outliers for data evaluation and validation may be accomplished using statistical procedures, such as the optional one provided in the DQCALC software, or through visual examination of a graphical representation of the data. WQE computations must be based on retained data from at least six independent measurements at each of at least five concentration levels. The data removed and the percentage of data removed must be recorded and retained to document the WQE calculations.

6.4 *Modeling Standard Deviation versus True Concentration*—The purpose is to characterize the intralaboratory measurement standard deviation (ILSD) as a function of true concentration, $\sigma = G(T)$. The relationship is used for two purposes: (*1*) to provide weights (if needed) for fitting the mean-recovery model and (*2*) to provide the within-laboratory standard deviation estimates crucial to determining the WQEs.

NOTE 3—See Caulcutt and Boddy (**5**) for more discussion of standard deviation modeling and weighted least squares (WLS) in analytical chemistry.

6.4.1 This practice utilizes four models as potential fits for the IntraLaboratory Standard Deviation (ILSD) model. The identification process considers (that is, fits and evaluates) each model in turn, from simplest to most complex, until a suitable model is found. See Carroll and Ruppert (**6**) for further discussion of standard-deviation modeling. The model order is as follows:

$$Model\ A\ (Constant\ ILSD\ Model):\quad s = g + \text{error} \tag{1}$$

where:

g = a fitted constant.

Under Model A, standard deviation does not change with concentration, resulting in a relative standard deviation that declines with increasing T.

$$Model\ B\ (Straight-line\ ILSD\ Model):\quad s = g + h \times T + \text{error} \tag{2}$$

where:

g *and* h = fitted constants.

Under Model B, standard deviation increases linearly with concentration, resulting in an asymptotically constant relative standard deviation as T increases.

$$Model\ C\ (Hybrid\ ILSD\ Model):\quad s = \{g^2 + (h \times T)^2\}^{1/2} + \text{error} \tag{3}$$

where:

g *and* h = fitted constants.

Under Model D, within-laboratory standard deviation increases with concentration in such a way that the relative standard deviation declines as T increases, approaching an asymptote of h.

$$Model\ D\ (Exponential\ ILSD\ Model):\quad s = g \times exp\ \{h \times T\} + \text{error} \tag{4}$$

where:

g *and* h = fitted constants.

Under Model D, within-laboratory standard deviation increases exponentially with concentration, resulting in a relative standard deviation that may initially decline as T increases, but eventually increases as T increases.

6.4.1.1 In all cases, it is assumed that $g > 0$. A value of $g < 0$ has no practical interpretation and may indicate that a different ILSD model should be used. Furthermore, it is assumed that g is not underestimated by censored data among measurements of blanks or other low-concentration samples. If $h < 0$, it must not be statistically significant, and Model A should be evaluated.

6.4.2 The ASTM D19 Practice D7510 describes the DQCALC software that can be used to perform the calculations for each of the four models, as well as the fit of each (this product can be obtained by contacting ASTM and asking for the DQCALC adjunct). The software identifies which model produced the best fit, and allows the user to select either this model or an alternative model. The software provides various graphical representations of the data and residuals, and the user manual provides assistance in using and interpreting the graphics and calculated values. Evaluation of the fit of each model to the data (as well as knowledge of chemistry, the method, and the systems used to generate the data) and judgment are important when selecting the most appropriate model. Where a model other than the best fit is chosen, the

reason for the choice should be scientific and should be recorded to document the WQE.

6.4.2.1 Users of this practice not using the ASTM D19 DQCALC software can consult Practice D6091, which contains a protocol that provides the full procedural, consensus-balloted basis for these calculations. It is also recommended that those not using the software graph the relationship of true concentration to measurement standard deviation, and visually verify the appropriateness of each model and of the model selected for use.

6.5 *Fitting the Mean-Recovery Relationship (Measured versus True Concentration)*—Based on the standard-deviation model selected (constant versus other models), the mean-recovery concentration is fitted versus true concentration, using ordinary least squares or weighted least squares, respectively. The mean-recovery is evaluated for statistical significance and lack of fit. A graph of mean recovery (along with the "calibration" line) and a graph of the residuals should also be visually examined. The ASTM D19 DQCALC software performs these activities automatically. Alternatively, many off-the-shelf statistical software packages may also be used.

NOTE 4—Regression coefficients should not be used to assess goodness of fit.

6.5.1 The mean-recovery regression (true versus measured concentration) model is a simple straight line,

$$\textit{Model R:}\quad Y = a + b\,T + \text{error} \tag{5}$$

The fitting procedure depends on the standard-deviation-model selection. If the constant model, Model A, was selected, then ordinary least squares (OLS) can be used to fit Model R for mean recovery (see the left column of Table 1, or Caulcutt and Boddy (**5**)). If a non-constant standard-deviation model was selected, then weighted least squares (WLS) should be used to fit mean recovery. The WLS approximately provides the minimum-variance unbiased linear estimate of the coefficients, *a* and *b*. The WLS procedure is described in the IDE Practice D6091.

6.6 *Compute the WQE for each Z (%RSD)*—Using the mean-recovery regression line determined above, the most appropriate model of the relationship of relative standard deviation to true concentration (also determined above), and the Z value desired, the user obtains the WQE, which is the true concentration (corresponding to the measured concentration) at which the desired % RSD was achieved.

TABLE 1 Ordinary Least Squares (OLS) and Weighted Least Squares (WLS) Computations to Estimate Straight-line Model Coefficients
(Computations shown for convenience and contrast)

OLS	WLS
$\bar{T} = 1/n\ \Sigma_{i=1}^{n}\ T_i$	$\bar{T}_w = 1/n\ \ \Sigma_{i=1}^{n}\ w_i T_i$
$y = 1/n \Sigma_{i=1}^{n} y_i$	$y_w = 1/n \Sigma_{i=1}^{n}\ w_i y_i$
$S_{TT} = \Sigma_{i=1}^{n} (T_i - \bar{T})^2$	$S_{wTT} = \Sigma_{i=1}^{n}\ w_i\ (T_i - \bar{T})^2$
$S_{TY} = \Sigma_{i=1}^{n}\ (T_i - \bar{T})\ (y_i - \bar{y})$	$S_{wTY} = \Sigma_{i=1}^{n}\ w_i (T_i - \bar{T})\ (y_i - \bar{y})$
slope $= b = S_{TY}/S_{TT}$	slope $= b = S_{wTY}/S_{wTT}$
intercept $= a = \bar{y} - b\bar{T}$	intercept $= a = y_w - b\bar{T}_w$

6.6.1 The measured concentration (YQ) at which the desired % RSD was achieved may also be of interest for some uses. This value is the level at which the required % RSD was obtained in measured concentration units (that is, the value, paired with a WQE, that has not been corrected for bias through the mean-recovery regression). Where the YQ and the WQE are equal (following application of significant figures and rounding), there is no bias present at the WQE concentration.

6.6.2 The WQE is the lowest true concentration at which (based on the modeling of standard deviation at that concentration and including the required confidence for the sample size (90% tolerance interval)) the percent relative standard deviation is achieved at the desired Z. The DQCALC adjunct software calculates the 10 %, 20 %, and 30 % WQE as the typical Z values.

6.6.2.1 Fig. 1 provides an example that demonstrates a case with positive bias (intercept greater than zero) and imperfect recovery (slope of the calibration not equal to one), thereby highlighting the advantages of the WDE procedure. More simplistic quantitation procedures often make inappropriate assumptions about slope (that is, assume it to be one) and y-intercept (that is, assume it to be zero at a true concentration of zero), in addition to assuming that the standard deviation is constant. Additionally, where the simplest model (constant) for standard deviation is rejected, the WDE procedure requires that weighted least squares be used for fitting the recovery model, thus preventing higher concentrations from having an excessive effect on the resulting curve; most other practices do not offer this protection.

7. Review, Documentation and Reporting

7.1 The WQE analysis report should include: (*1*) the identification of laboratory and (*2*) identification of analytical method, analyte(s), matrix (or matrices), sample properties (for example, volume or mass) and specific method options (if any) utilized. Where the laboratory uses standard operating procedures (SOPs) to implement methods or method protocols, these SOPs should be referenced, including the identification of any revision/version. Documentation of each datum used should be equivalent to that of reported data (for example, instrument, analyst, date, etc.). There should be a description of all data-screening procedures employed, all results obtained, all individual values omitted from further analysis (that is, outliers that have been removed), all missing values, and the percentage of data utilized in the calculations relative to the initial data set. Any anomalies encountered should be listed, including and anomalous calibration or quality control sample results (for example, data validation qualifiers or flags). The data (statistical) analysis should be included or referenced (for example, the output file from the DQCALC software) and the WQE values determined recorded. The selected standard-deviation model, plus the coefficient estimates for this model and for mean-recovery model, should also be recorded. Where a statistical model other than the mathematical best fit has been chosen, the reasoning should be described.

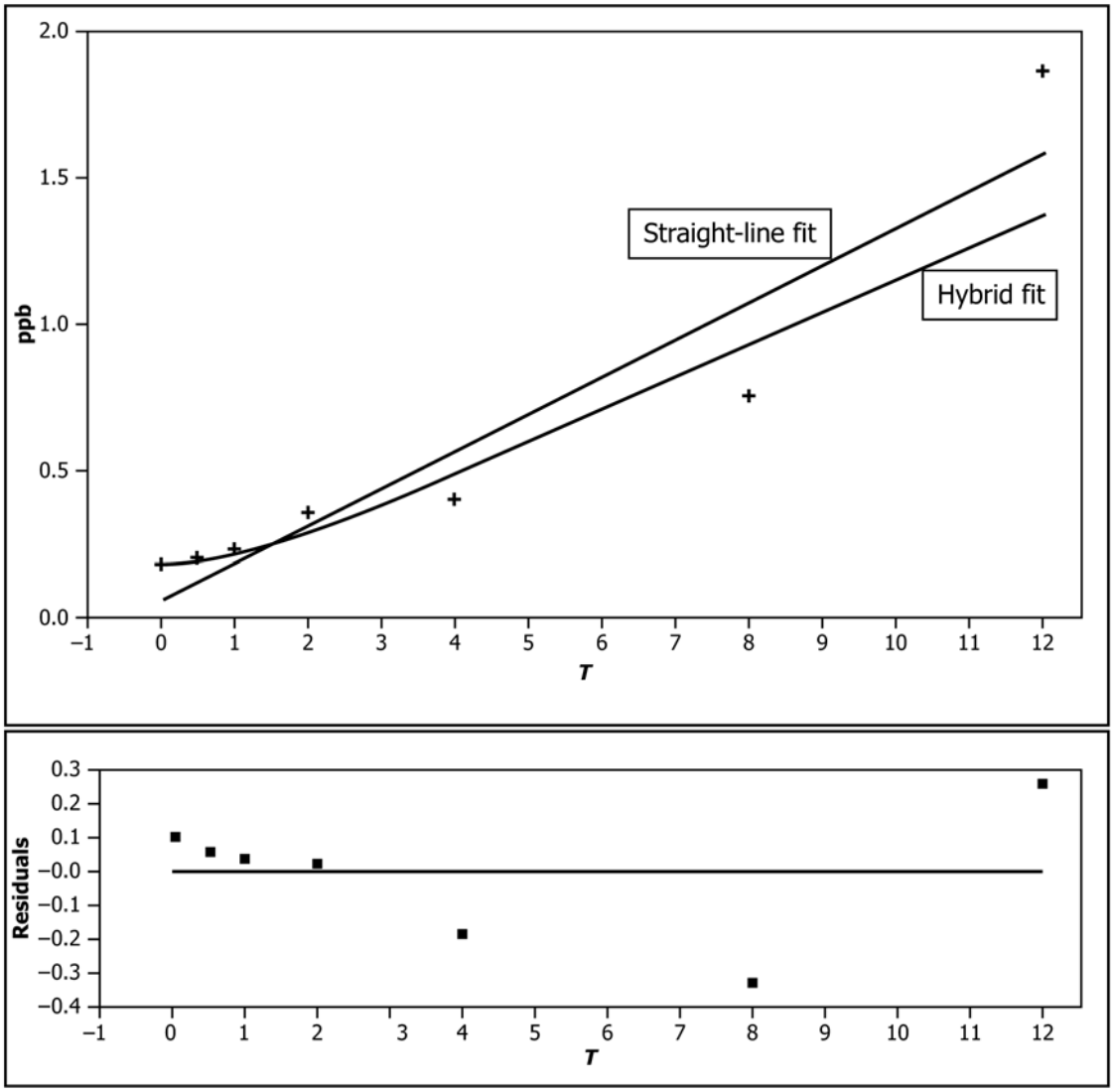

FIG. 1 Sample Standard Deviations (+) Versus True Concentration, with Straight-Line Fit, Hybrid Model Fit, and Residuals from Straight-Line Fit (Lower Plot), All in ppb

8. Report

8.1 The analysis report should at a miminum contain:

8.1.1 Identification of laboratory,

8.1.2 Analytical method,

8.1.3 Analyte(s),

8.1.4 Matrix (or matrices),

8.1.5 Sample properties (for example, volume),

8.1.6 Study design,

8.1.7 Analyst, method, and date of testing for each study sample,

8.1.8 Any anomalies in the study, including QA/QC sample results,

8.1.9 Data-screening results, individual values and laboratories omitted from further analysis, and missing values,

8.1.10 ILSD model selected, and

8.1.11 Coefficient estimates for the ILSD model and mean-recovery model.

NOTE 5—The DQCALC input and output files provide much of this documentation.

8.2 The report should be given a second-party review to verify that:

8.2.1 The data transcription and reporting have been performed correctly,

8.2.2 The analysis of the data and the application of this standard have been performed correctly, and

8.2.3 The results of the analysis have been used appropriately, including assessment of assumptions necessary to compute a WQE.

NOTE 6—Reviewer(s) should be qualified in one or both of the following areas: (*1*) applied statistics, and (*2*) analytical chemistry.

8.3 A statement of the review and the results of the review should accompany the report.

9. Rationale

9.1 The basic rationale for the WQE is contained in Currie (**1**). The WQE is a performance characteristic of an analytical method, to paraphrase Currie. As with the Within-Laboraotory Detection Estimate (WDE), the WQE is helpful for the

planning and use of chemical analyses. The WQE is another benchmark indicating whether the method can adequately meet measurement needs.

9.2 The idealized definition of $WQE_{Z\ \%}$ is that it is the lowest concentration, LQ, that satisfies: $T = (100/Z)\ \varsigma_T$ (where ς_T is the actual standard deviation of interlaboratory measurements at concentration T); this definition is equivalent to satisfying, % RSD = ς_T/T = Z %. In other words, $WQE_{Z\ \%}$ is the lowest concentration with Z % RSD (assuming such a concentration exists). If, as is commonly the case, % RSD declines with increasing true concentration, then the relative uncertainty of any measurement of a true concentration greater than the WQE will not exceed ±Z %. The range, $\pm 3\varsigma_{LQ}$, is an approximate prediction or confidence interval very likely to contain the measurement, which is assumed to be normally distributed. This assertion is based on critical values from the normal distribution (or from the student's t distribution if ς is estimated rather than known). Then, with high confidence, the relative error of any measurement of a true concentration greater than the WQE will not exceed $\pm 3 \cdot$ Z %. For example, a measurement above the $WQE_{10\ \%}$ (and assumed to have true concentration above the WQE) could be reported as 6 ppb (±30 %) = 6 (±2) ppb, with a high degree of certainty.

9.3 There are several real-world complications to this idealized situation. See Maddalone et al (**7**), Gibbons (**8**), and Coleman et al (**9**). Some of these complications are listed as follows:

9.3.1 Analyte recovery is not perfect; the relationship between measured values of concentrations and true concentrations cannot be assumed to be trivial. There is bias between true and measured values. Recovery can and should be modeled. Usually a straight line will suffice.

9.3.2 Variation is introduced by different laboratories, analysts, models and pieces of equipment; environmental factors; flexibility/ambiguity in a test method; contamination; carryover; matrix influence; and other factors. It is intractable to model these factors individually, but their collective contributions to measurement ILSD can be observed, if these contributions are part of how a study is designed and conducted.

9.3.3 The standard deviation of measurements is generally unknown, and may change with true concentration, possibly because of the physical principle of the test method. To ensure that a particular % RSD is attained at or above the WQE, there must be a way to predict the ILSD at different true concentrations. Short of severely restricting the range of concentrations for a study, prediction is accomplished by an empirical ILSD model. In all of the respects discussed in 9.1 – 9.3, $WQE_{10\ \%}$ is similar to the AML developed by Gibbons et al (**10**). However, the AML follows an approximate approach, where the standard deviation used in the 10ς formula is estimated at a detection critical value, and then is taken to be a constant (over a trace-level range of concentrations) for the 10ς computation. In contrast, $WQE_{10\ \%}$ follows the "more statistically and conceptually rigorous" approach described by Gibbons et al (**8**), and contained in Currie (**1**). This greater rigor comes at the risk of: (*a*) possibly being unattainable for some methods (for which only a less strict level of % RSD can be ensured); (*b*) having uncertainty that is potentially complex, and depends both on the model used and on the data.

10. Keywords

10.1 critical limits; matrix effects; precision; quantitation; quantitation limits

APPENDIXES

(Nonmandatory Information)

X1. GLOSSARY OF KEY SYMBOLS, ACRONYMS, AND LABELS

ς—true interlaboratory standard deviation

Δ*g*—one iteration's change in the estimate of *g*, the intercept coefficient in the Hybrid model

Δ*h*—one iteration's change in the estimate of *h*, the slope coefficient in the Hybrid model

a—estimate of the slope in the mean-recovery curve (straight-line model)

a[prime]$_n$—adjustment factor used to remove bias from the sample interlaboratory standard deviation

AML—Alternative Minimum Level, a quantitation limit that is similar to the WQE (and compatible in approach)

b—estimate of the slope in the mean-recovery curve (straight-line model)

b[prime]—crude estimate of *b*

c–intermediate variable used in estimating *g* and *h* for the Hybrid model, by nonlinear least squares. Similar to *d, p, q, u*, and *v*

D—difference between *T* and ((100/Z)·(estimated interlaboratory standard deviation)), used for approximate, graphical determination WQE

d—similar to *c*

f(T)—the natural log of the current estimate of the interlaboratory standard deviation at concentration, *T*

g—estimate of the intercept in the Hybrid model of interlaboratory standard deviation

G(T)—the (generic) model of the interlaboratory standard deviation go—initial estimate of *g*

IDE—the interlaboratory detection estimate, defined and described in Practice D6091

ILSD—interlaboratory standard deviation

$WQE_{Z\%}$—interlaboratory quantitation estimate associated with approximately Z % RSD

j—iteration index used for nonlinear least squares solution of the coefficients for the Hybrid model for ILSD

k—index used for different concentrations, T_k, and associated statistics

LQ—Another designation for the WQE, in accordance with Currie's notation

Model A—Constant model for ILSD

Model B—Straight-line model for ILSD; interlaboratory standard deviation increases with increasing concentration

Model C—Hydrid model for ILSD; combines additive and multiplicative error, with interlaboratory standard deviation that increases with increasing concentration, according to the model proposed by Rocke and Lorenzato

Model R—the straight-line model for the mean-recovery curve

NLLS—nonlinear least squares, where coefficients in a nonlinear model are computed to minimize the sum of the squares of the residuals (that is, the differences between the predicted and actual values)

OLS—ordinary least squares, a fitting technique for a linear (that is, additive) model that minimizes the sum of the squares of the residuals (that is, the differences between predicted and actual values)

p—similar to *c*

q—similar to *c*

q_k—k^{th} value in the T^2 quadratic component that is orthogonal to *T*

Q—intermediate variable used in ILSD model selection, to test for statistically significant curvature

QL—quantitation limit (also called practical quantitation limit, PQL); see LQ

r—the estimated lowest limit of % RSD achievable, based on study results, for a particular measurement system, matrix, and analyte

r_k(unrelated to *r*)—the residual associated with T_k from a precision model fit; defined as the difference in log sample standard deviation and log estimated (predicted) standard deviation

RSD—relative standard deviation, that is, the standard deviation divided by the concentration, (both generally estimated)

s—modeled value of the interlaboratory standard deviation, including error

s_k—sample interlaboratory standard deviation at true concentration, T_k, adjusted to remove bias

s_{max}—maximum sample ILSD: equal to max \s_1, s_2, . . .\

T—true concentration

T_k—k^{th} value of true concentration in the study

T_{max}—maximum concentration in the study; equal to max \T_1, T_2, ...\

WLS—weighted least squares, a modified form of ordinary least squares. WLS incorporates nonuniform variability in the data

Y—random variable representing a reported measurement

Z—level of RSD

X2. FITTING THE HYBRID (ROCKE AND LORENZATO (3)) MODEL FOR ANALYTICAL MEASUREMENTS, USING NEWTON'S METHOD OF NON-LINEAR LEAST SQUARES (NLLS)

X2.1 The following numerical procedure can be conveniently carried out by using computer spreadsheet software:

X2.1.1 *Initialize*—The index, *j*, is the step number for iteration. Set *j*=0.

X2.1.1.1 Compute the natural log of the sample standard deviation, ls_k, for each true concentration, T_k.

NOTE X2.1—The log transformation standardizes the residuals so that the sum of squares of logs of relative errors is minimized. Log-relative errors are preferred to absolute errors, since the latter are almost certainly unequal in variation.

X2.1.1.2 Compute initial values, g_0 and h_0, as follows:

g_0 = s_1(the sample standard deviation for the lowest concentration, T_1; usually T_1=0)

h_0 = $(s_{max} - s_1) / (T_{max} - T_1)$ if $s_{max} > s_1$, where s_{max} is the maximum sample standard deviation of measurements, made at concentration,T_{max}. Otherwise, set $h_0 = 0$.

X2.1.1.3 Compute the natural log of the estimated standard deviation, lss_k, for each T_k, using the current estimates, g_j and h_j:

$$lss_k = f(T_k) \tag{X2.1}$$

where we define

$$f(T_k) = ln\sqrt{g_j^2 + h_j^2 T_k^2}$$

X2.1.1.4 Compute the difference (residual), r_k, between the log sample standard deviation and estimated log standard deviation for each *k*:

$$r_k = ls_k - lss_k \tag{X2.2}$$

Note that r_k is the natural log of the ratio of the sample standard deviation to the estimated standard deviation, so r_k represents log-proportional error, and is ideally equal to zero.

X2.1.1.5 Compute f_{gk}, the slope (that is, numerical derivative) of *f(T)* with respect to *g*, for each *k*:

$$fg_k = g_j / exp\{2\ lss_k\} \tag{X2.3}$$

X2.1.1.6 Compute fh_k, the slope of *f(T)* with respect to *h*, for each T_k:

$$fh_k = h_j (T_k)^2 / exp\{2\ lss_k\} \tag{X2.4}$$

X2.1.1.7 Compute the following intermediate statistics:

$u = \sum_k (fg_k)^2$ $\quad v = \sum_k (fh_k)^2$ $\quad c = \sum_k (fg_k \cdot fh_k)$

$d = 1/uv - c^2$ $\quad p = \sum_k (fg_k \cdot r_k)$ $\quad q = \sum_k (fh_k \cdot r_k)$

X2.1.1.8 Compute the *j*th step changes to *g* and *h* (made to reduce the sum of squared residuals), and % relative changes:

$\Delta g = d\ (vp - cq)$ $\quad dg\% = 100\ |\Delta g / g_j|$

$\Delta h = d\ (uq - cp)$ $\quad dhT\% = 100\ |\ \Delta h / h_j| T_{max}$

X2.1.1.9 Compute new *g* and *h* estimates:

$$g_{j+1} = g_j + \Delta g \tag{X2.5}$$

X2.1.1.10 If $dg\% < 1\ \%$ and $dhT\% < 1\ \%$, then stop and use g_{jh} and h_{jh} as the final estimates. Otherwise, increase j by 1, and go to X2.1.1.3.

X3. THREE WLS APPROXIMATIONS TO BE AVOIDED

X3.1 There are three approximate approaches to WLS commonly used, but not acceptable for this practice. One approach uses the reciprocal-squared sample standard deviations, s_k^{-2}, as weights. Since this practice involves the explicit evaluation and selection of a standard-deviation model, the predicted value for s_k is probably more precise than a sample value, and the former value should be used to compute weights. A second approach omits the blank measurements, and divides the rest of the measurements by the true concentrations. Then, OLS is carried out, using the independent variable, $1/T$, in the following model:

$$Y/T = a\,(1/T) + b + \text{error} \qquad \text{(X3.1)}$$

This approach is not acceptable because it leads to loss of data and because the weights so generated implicitly assume that interlaboratory standard deviation is strictly proportional to true concentration. A proportional relationship cannot hold for arbitrarily small concentrations. The third approach exploits the same approximate (but untrue) proportional relationship to obtain mathematically simpler WLS formulas.

X4. EXAMPLE

X4.1 *Identify and Fit the ILSD Model*—Measurements were made at each of seven concentrations: *Tk* = \0.0, 0.50, 1, 2, 4, 8, 12\ ppb.

X4.1.1 The reported measurements are shown in Table X4.1. These values are also shown in Fig. X4.1. The straight-line recovery model appears to be plausible for the mean-recovery model, and the data appear to have measurement ILSDs that increase with concentration.

X4.1.2 The standard deviations at each true concentration are computed, adjusted for bias (Table X4.2) and are shown in Table X4.1.

X4.1.3 A plot of standard deviation versus true concentration is shown in Fig. 1. The plot provides additional qualitative evidence of an increase in standard deviation with increasing concentration.

X4.1.4 A straight-line regression (using OLS) is initially conducted of the standard deviations (s_k) versus T_k. The results are shown in Table X4.3, and the fit is shown in Fig. 1.

X4.1.5 The slope estimate, h, is statistically significant with a p-value of $0.0012 < 5\ \%$, so the Constant ILSD model (Model A) is rejected.

TABLE X4.1 Reported Measurements and Computed Statistics from the Example WQE Study

True Concentration T_k, ppb	Reported Measurement Values, y_i	s_k = Standard Deviation (adjusted)	$ln\ s_k$	$[scirc]_k$ = Predicted Standard Deviation (Hybrid Model)	WLS Weights: $w_k = ([scirc]_k)^{-2}$	q_k, Orthogonal Component of $(T_k)^2$
0	–0.105, 0.263, 0.293, 0.187, 0.106, 0.329, 0.080, 0.524, 0.278, 0.206	0.1729	–1.7549	0.1840	20.54	13.029
0.5	0.354, 0.724, 0.682, 0.327, 0.527, 0.868, 0.730, 0.434, 0.794, 0.642	0.1929	–1.6454	0.1927	26.93	7.453
1	1.241, 0.668, 1.200, 1.370, 1.106, 0.964, 0.949, 1.421, 1.032, 1.134	0.2270	–1.4829	0.2168	21.28	2.376
2	2.174, 2.388, 2.153, 2.366, 2.306, 2.309, 1.663, 2.841, 1.933, 1.809	0.3449	–1.0644	0.2939	11.58	–6.277
4	3.660, 3.734, 3,167, 3.578, 4.278, 3.383, 3.873, 4.479, 3.919, 3.856	0.3995	–0.9175	0.4940	4.10	–17.582
8	6.592, 7.520, 6.822, 7.751, 7.771, 7.296, 8.578, 6.863, 7.840,8.821	0.7521	–0.2849	0.9351	1.14	–16.194
12	9.496, 9.081, 13.942, 10.547, 9.324, 13.148, 10.994, 11.774, 12.320, 13.521	1.8519	0.6162	1.3875	0.52	17.194

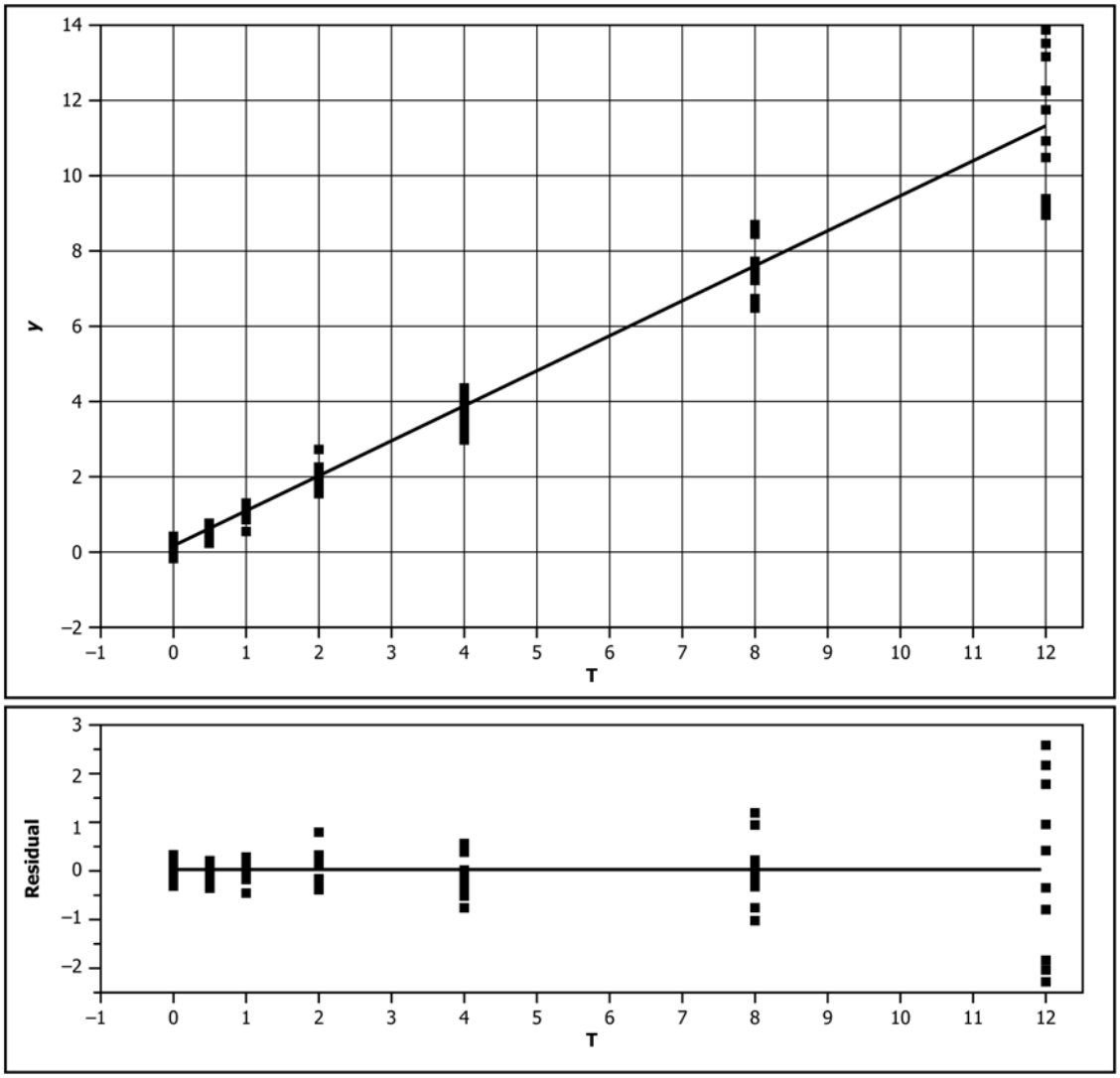

FIG. X4.1 Reported Concentration Measurement (ppb) Versus True Concentration (ppb); Each Concentration With Weighted Least Square-Line Fit (above) and (below) Residuals

TABLE X4.2 Bias-Correction Adjustment Factors for Sample Standard Deviations Based on *n* Measurements (at a particular concentration)[A]

n	2	3	4	5	6	7	8	9	10
$a[prime]_n$	1.2	1.1	1.0	1.064	1.0	1.0	1.036	1.0	1.0
	53	28	85		51	42		31	28

[A]For each true concentration, T_k, the adjusted value $s_k = a[prime]_n s[prime]_k$ should be modeled in place of sample standard deviation, $s[prime]_k$. For $n > 10$, use the formula, $a[prime]_n = 1 + [4(n\text{-}1)]\text{-}1$. See Johnson and Kotz (**11**).

TABLE X4.3 Straight-Line OLS Fit of *s* on *T*

Standard Deviation = $s = g + hT = 0.06498 + 0.12678\ T$

Summary of Fit

RSquare	0.896432
RSquare Adj	0.875719
Root Mean Square Error	0.212178

Parameter Estimates

Term	Estimate	Standard Error	*t*-Ratio	Prob > |t|
g	0.064976	0.110288	0.59	0.5814

X4.1.6 The reasonableness of the straight-line model (Model B) is evaluated using the lower plot (in Fig. 1) (that is, the plot of residuals versus true concentration). There is subjective appearance of systematic curvature (a roughly U-shape to the residuals).

X4.1.7 To assess more formally the need for a model with curvature (Hybrid, Model C) instead of the straight line model (Model B), a formal test is conducted.

X4.1.7.1 Using OLS, $(T_k)^2$ is regressed on T_k, producing residuals, q_k, shown in Table X4.1.

X4.1.7.2 Using OLS, s_k is regressed on T_k and q_k together, once again producing estimates of coefficients g and h, and additionally Q, the coefficient of q. The results are shown in Table X4.4.

X4.1.7.3 From Table X4.4, it can be seen that $p_Q = 0.0096 < 5\ \%$, and $Q = 0.013 > 0$, so there is sufficient evidence of curvature to warrant using the Hybrid Model (Model C).

TABLE X4.4 Summary of OLS Fit of *s* on *T* and *q*

Term	Estimate	SI	*t* Ratio	Prob>|t|
g (Intercept)	0.0649765	0.048621	1.34	0.2524
h (slope *w.r.t. T*)	0.1267813	0.008496	14.92	0.0001
Q (coefficient of *q*)	0.0129282	0.002774	4.66	0.0096

X4.1.8 Model C, the Hybrid Model, is used to fit the sample standard deviation data in Table X4.1, using NLLS solved by Newton's-method iteration, as presented in the appendix. The steps are as follows:

X4.1.8.1 Compute the natural log sample standard deviation, ls_k, for each true concentration, T_k. See Table X4.1.

X4.1.8.2 Let j be the index of iteration, and set j=0. Compute initial values, g_0 and h_0, as follows:

$$g_0 = s_1 = 0.173 \quad \text{(X4.1)}$$

$$h_0 = (s_{max} - s_1)/(T_{max} - T_1) = 0.140 \quad \text{(X4.2)}$$

See Table X4.5.

X4.1.8.3 Compute the natural log of the estimated standard deviation, lss_k, for each k, using the current values of g_j and h_j (not shown).

X4.1.8.4 Compute the residuals $r_k = ls_k - lss_k$ for each k (not shown).

X4.1.8.5 Compute $fg_k = g_j/exp\backslash 2\ lss_k\backslash$ for each k (not shown).

X4.1.8.6 Compute $fh_k = h_j(Tk)^2/\ exp\backslash 2\ lss_k\backslash$ for each k (not shown).

X4.1.8.7 Compute intermediate statistics: *u, v, c, d, p,* and *q*. See Table X4.5.

X4.1.8.8 Compute the *j*th-step changes to *g* and *h* (see Table X4.5):

$$\Delta g = d\ (Vp - cq) \qquad dg\% = 100\ |\Delta g\ /\ gj|$$

$$\Delta h = d\ (Uq - cp) \qquad dhT\% = 100\ |\Delta\ hj|Tmax$$

X4.1.8.9 Compute the new g and h (see Table X4.5):

$$g_{j+1} = g_j + \Delta g \qquad h_{j+1} = h_j + \Delta h$$

X4.1.8.10 Iterate (increase j by 1, and return to X4.1.8.3) until $dg\% < 1$ % and $dhT\% < 1$ %.

X4.1.8.11 As can be seen in Table X4.5 for j=2, $dg\%$=0.02 % < 1 % and dhT %=0.2 % < 1 %, so convergence is achieved after the second step of iteration, with g=0.184 and h=0.1146.

X4.1.8.12 As seen in Table X4.1, the coefficients, g and h, are used to compute a predicted measurement standard deviation, $[scirc]_k$, at each of the T_k values. The $[scirc]_k$ values are then used to compute weights, w_k, also seen in Table X4.1.

X4.1.9 WLS uses the weights, w_k, to fit the straight-line mean-recovery function. The results are shown in Table X4.6.

X4.1.10 Finally, compute WQE_Z %. First, the lowest achievable %RSD is estimated, in accordance with the formula for the Hybrid Model: Z[prime] = $100h/b = 100 \cdot 0.1146/0.931 = 12$, which is rounded up to a whole-number multiple of 10: Z=20. Hence, $WQE_{20\ \%}$ can be computed (but not $WQE_{10\ \%}$), as follows:

$$WQE_{20\ \%} = g/\left[(b\cdot 20/100)^2 - h^2\right]^{(1/2)} = 0.184/\left[(0.931\cdot 20/100)^2 - 0.1146^{1/2}\right] = 1.254\ ppb \quad \text{(X4.3)}$$

For comparison purposes, a simple, model-free quantitation limit equal to five times the sample measurement's standard deviation from blank replicates might be $5 \cdot sl = 5 \cdot 0.173 = 0.865$ ppb. This estimate would be even lower if an intralaboratory standard deviation were used instead of an interlaboratory standard deviation.

X4.1.11 It is also possible to compute $WQE_{30\ \%}$, as follows:

$$WQE_{30\ \%} = g/\left[(b\cdot 30/100)^2 - h^2\right]^{(1/2)} \quad \text{(X4.4)}$$

$$= 0.184/\left[(0.931\ \cdot\ 30/100)^2 - 0.1146^2\right]^{(1/2)} = 0.722\ \text{ppb}$$

TABLE X4.5 Summary Statistics from Newton's Method Fit of Hybrid Model

j	*g*	*h*	*u*	*v*	*c*	*d*	*p*	*q*	Δ*g*	Δ*h*	*dg%*	*dh T%*
0	0.173	0.1400	73.11	176.87	27.77	8.22E–05	0.0634	–4.3765	0.0109	–0.0265	6.3	227
1	0.183	0.1135	74.99	238.43	32.28	5.96E–05	0.0540	0.2681	0.0002	0.0011	0.1	11.5
2	0.184	0.1146	74.47	234.83	32.89	6.10E–05	–0.0016	0.0037	–3E05	2E–05	0.02	0.2

TABLE X4.6 WLS Straight-Line Fit for Measured Values Versus True

Measurement = $y = 0.19399 + 0.93062T$
Measurement = $y = a + bT$

Summary of Fit

RSqu	0.963246
RSquare Adj	0.962706
Root Mean Square Error	0.994013

Parameter Estimates

Term	Estimate	Standard Error	*t* Ratio	Prob>|t|
a (intercept)	0.1939874	0.038359	5.06	< 0.0001
b (slope)	0.9306236	0.022045	42.22	< 0.0001

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