



Standard Practice for Determination of the 99 %/95 % Critical Level (WCL) and a Reliable Detection Estimate (WDE) Based on Within- laboratory Data¹

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1. Scope

1.1 This practice provides a procedure for computing a 99 %/95 % Within-laboratory Detection Estimate (WDE) and the associated critical level/value (WCL). The WDE is the minimum concentration, with false positives and false negative appropriately controlled, such that values above these minimums are reliable detections. The WCL is the point at which only false positives are controlled appropriately. A false positive is the reporting of an analyte as present when the analyte is not actually present; false negatives are reports of analyte absence when the analyte is actually present. This practice is distinguished from the Interlaboratory Detection Estimate (IDE) practice in that the IDE Standard utilizes data from multiple, independent laboratories, while this practice is for use by a single laboratory. The IDE would be utilized where interlaboratory issues are of concern (for example, limits for published methods); this practice (and values derived from it) are applicable where the results from a single laboratory, single operator, single instrument, etc. are involved (for example, in understanding, censoring and reporting data).

1.2 The establishment of a WDE involves determining the concentration below which the precision and bias of an analytical procedure indicates insufficient confidence in false-positive and false-negative control to assert detection of the analyte in the future analysis of an unknown number of samples. Most traditional approaches attempt to determine this detection “limit” by estimating precision at only a single, arbitrary point. The WDE approach is intended to be a more technically rigorous replacement for other approaches for estimating detection limits. The WDE practice addresses a number of critical issues that are ignored in other approaches.

1.2.1 First, rather than making a single-point estimate of precision, the WDE protocol requires an estimate of precision

at multiple points in the analytical range, especially in the range of the expected detection limit. These estimates are then used to create an appropriate model of the method’s precision. This approach is a more credible way to determine the point where relative precision has become too large for reliable detection. This process requires more data than has been historically required by single-point approaches or by processes for modeling the relationship between standard deviation and concentration.

1.2.2 Second, unlike most other approaches, the WDE process accounts for analytical bias at the concentrations of interest. The relationship of true concentration to measured concentration (that is, the recovery curve) is established and utilized in converting from as-measured to true concentration.

1.2.3 Third, most traditional approaches to detection limits only address the issue of false positives. Although false negatives may not be of concern in some data uses, there are many uses where understanding and/or control of false negatives is important. Without the false-negative-control information, data reported with just a critical-level value are incompletely described and the qualities of data at these levels incompletely disclosed.

1.2.4 Fourth and last, the WDE standard utilizes a statistical-tolerance interval in calculations, such that future measurements may reasonably be expected to be encompassed by the WDE 90 % of the time. Many older approaches have used the statistical confidence interval, which is not intended to encompass individual future measurements, and has been misunderstood and misapplied. Procedures using the confidence interval cannot provide the stated control when the detection-limit value is applied to future sample results; such application is the primary use of these values.

1.3 To summarize, the WDE is computed to be the lowest true concentration at which there is 90 % confidence that a single (future) measurement (from the studied laboratory) will have a true detection probability of at least 95 % and a true non-detection probability of at least 99 % (when measuring a blank sample). For the laboratory in the study, the critical value

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is the true concentration at which, on average, (with approximately 90 % confidence) will not be exceeded by 99 % of all measurements of samples with true concentration of zero (that is, blanks). These values are established by modeling the precision and establishing the recovery/bias over a range of concentrations, as well as by using a tolerance interval. The complexities of the WDE procedure may appear daunting, but the additional considerations are necessary if meaningfully estimates of the actual detection capabilities of analytical methods are to be made. The concepts are tractable by degreed chemists, and the use of the available ASTM DQCALC Excel-based software makes the data analysis and limit determinations easy.

1.4 A within-laboratory detection estimate is useful in characterizing the concentration below which a method, for an analyte, as implemented in a specific laboratory, does not (with high confidence) discriminate the presence of the analyte from that of the absence of an analyte. As such an estimator, the WDE Standard (and the WDE and WCL values produced through its application) are useful where a trace-analysis testing method needs to be used.

2. Referenced Documents

2.1 ASTM Standards:²

D1129 Terminology Relating to Water

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

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 *99 %/95 % Within-laboratory Detection Estimate, n —(99 %/95 % WDE, also denoted LD for Limit of Detection, analogous to Currie (1)³* The lowest concentration at which there is 90 % confidence that a single measurement from the laboratory studied will have a true detection probability of at least 95 % and a true non-detection probability of at least 99 %.

3.2.2 *Probability of False Detection (α), n —*The within-laboratory false-positive probability that a single measurement of a blank sample will result in a detection; see Fig. 1.

3.2.2.1 *Discussion*—This probability is often referred to as the Type-1-error probability; it depends on the analyte, measurement system, analytical method, matrix, analyst, and measurement (recovery) threshold (measurement critical value) used to decide whether detection has occurred.

3.2.3 *Probability of True Non-detection ($1-\alpha$), n —*The within-laboratory true-negative probability that a single measurement of a blank sample will result in a non-detection.

3.2.3.1 *Discussion*—This concept is the complement of the probability of false detection. (See Fig. 1) This probability also depends on the analyte, measurement system, analytical method, matrix, analyst, and response threshold.

3.2.4 *Probability of True Detection ($1-\beta$ or $1-\beta(T)$), n —*The within-laboratory probability that a single measurement of a sample containing a nonzero analyte concentration, T , will result in a detection; see Fig. 1.

3.2.4.1 *Discussion*—This probability: 1) is often referred to as statistical power or the power of detection, 2) depends explicitly on the concentration (T), and 3) depends implicitly on the analyte, measurement system, analytical method, matrix, analyst, and critical value for detection.

3.2.5 *Probability of False Non-detection (β or $\beta(T)$), n —*The within-laboratory false-negative probability that a single measurement of a sample containing a nonzero analyte concentration, T , will result in a non-detection.

3.2.5.1 *Discussion*—This concept is the complement of the probability of true detection. (See Fig. 1.) This probability function: 1) is often referred to as the Type-2-error probability function, 2) depends explicitly on the concentration (T), and 3) depends implicitly on the analyte, measurement system, analytical method, matrix, analyst, and critical value for detection.

² 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.

³ The boldface numbers in parentheses refer to a list of references at the end of this standard.

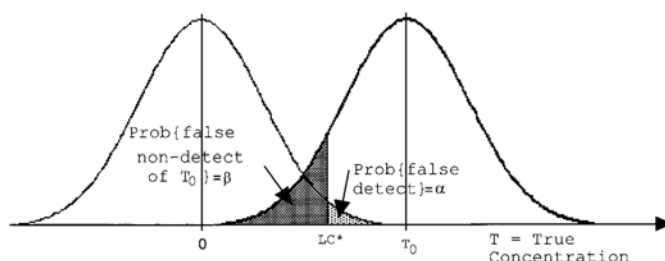


FIG. 1 Normal Distribution of Zero Concentration (without bias), Low Concentration (near zero) and Simplest Case of Reliable Detection

3.2.6 Detection Limit (DL) or Limit of Detection (LD), n —For the studied laboratory, a numerical value, expressed in physical units or proportion, intended to represent the lowest level of reliable detection (that is, a level that can be discriminated from zero with high probability, while simultaneously allowing high probability of non-detection when blank samples are measured).

3.2.7 Censored Measurement, n —A measurement that is not reported numerically or reported missing, but reported as a nondetect or a less-than (for example, “less than 0.1 ppb”).

3.2.7.1 Discussion—A non-zero report means that a measurement-system algorithm determined that the measurement should not be reported numerically because: 1) it was considered insufficiently precise or insufficiently unbiased, or 2) the identification of the analyte was suspect. A reported “less-than” may have the same meaning; however, such a report also implies (perhaps erroneously) that any concentration greater than or equal to the accompanying value (for example, 0.1 ppb) can be measured and will be reported numerically.

3.2.8 $100(1-\gamma)$ %—Confidence Statistical Tolerance Limit for $100(1-\delta)$ % of a Population (also known as a One-Sided Statistical Tolerance Interval), n —A statistically determined limit that will, with $100(1-\gamma)$ % confidence, exceed (or fall below) $100(1-\delta)$ % of the population (that is, the $100(1-\delta)$ % quantile). See Hahn and Meeker (2) for further explanation and tables of values.

3.3 Acronyms:

3.3.1 *ILSD*—Intralaboratory standard deviation

3.3.2 *WCL*

3.3.3 *WDE*

3.3.4 *YC*

3.3.5 *YD*

4. Summary of Practice

4.1 Data representative of the laboratory, method, and media at multiple (at least five) concentrations of the analyte, covering the range from zero (or near zero) to at or above the level of expected quantitation, are generated. The fundamental assumption is that the media tested, the concentrations tested, and the protocols followed are representative of the written test method as implemented in the laboratory. The WDE 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 The relationship between the within-laboratory measurement standard deviation and the true concentration is established by evaluating a series of potentially appropriate models, from simplest to most complex (that is, constant, straight-line, hybrid, and exponential). This evaluation of models includes statistical significance and residual analysis. A single model (selected by the user, based on statistical best-fit, visual review of fit and residuals, and judgment) is then used to predict within-laboratory measurement standard deviation at any true concentration.

4.3 If the within-laboratory standard deviation is not constant, weights must be generated for fitting the true versus

measured concentration relationship (that is, the straight-line relationship between measured concentration and true concentration, known as the mean-recovery relationship), using weighted least squares; software such as DQCALC will do this modeling. For constant standard deviation, ordinary least-squares is used to fit the mean-recovery relationship. The true-versus-measured linear fit is evaluated for statistical significance and behavior of the residuals.

4.4 The modeled within-laboratory standard deviation at zero concentration is used to compute YC, the measured concentration that (with 90% confidence) 99 % of samples with true concentrations of zero will be less than (that is, less than the YC). The YD is computed to be the measured concentration that (with approximately 90 % confidence) will produce measurements that will exceed YC at least 95 % of the time; simultaneously when blank samples are measured, YD will not exceed YC more than 1 % of the time (that is, will not exceed the reliable detection level, YD). In turn, the WCL and the WDE are the true concentrations corresponding to YC and YD, respectively, from the recovery regression.

4.5 While the application of this practice does require the use of statistics, the complex calculations are performed by the adjunct software, DQCALC. Practice D6091 provides the complete mathematical basis for the calculations. Appendix X1 provides an example WDE calculation.

5. Significance and Use

5.1 This practice can be used in a single laboratory for trace analysis (that is, where: 1) there are concentrations near the lower limit of the method and 2) the measurements system’s capability to discriminate analyte presence from analyte absence is of interest). In these testing situations, a reliable estimate of the minimum level at which there is confidence that detection of the analyte by the method represents true presence of the analyte in the sample is key. Where within-laboratory detection is important to data use, the WDE procedure should be used to establish the within-laboratory detection capability for each unique application of a method.

5.2 When properly applied, the WDE procedure ensures that the 99 %/95 % WDE has the following properties:

5.2.1 Routinely Achievable Detection—The laboratory is able to attain detection performance routinely, using studied measurement systems, without extraordinary effort, and therefore at reasonable cost. This property is needed for a detection limit to be practically useful while scientifically sound. Representative equipment and analysts must be included in the study that generates the data to calculate the WDE.

5.2.2 Inclusion of Routine Sources of Error—If appropriate data are used in calculation, the WDE practice will realistically account for sources of variation and bias common to the measurement process and routine for sample analysis. These sources include, but are not limited to: 1) intrinsic instrument noise, 2) some typical amount of carryover error, and 3) differences in analysts, sample preparation, and instruments (including signal-processing methods and software versions).

5.2.3 Exclusion of Avoidable Sources of Error—The WDE practice excludes avoidable sources of bias and variation, (that

is, those which can reasonably be avoided in routine field measurements). Avoidable sources would include, but are not limited to: 1) inappropriate modifications to the method, the sample, measurement procedure, or measurement equipment, and 2) gross and easily discernible transcription errors (provided there was a way to detect and either correct or eliminate such errors in routine sample testing).

5.2.4 Low Probability of False Detection—Consistent with a measured concentration threshold (YC), the WCL is a true concentration that will provide a high probability (estimated at 99 %) of true non-detection (and thus a low estimated probability of false detection (α) equal to 1 %). Thus, when a sample with a real concentration of zero is measured, the probability of not detecting the analyte (that is, the probability that the measured value of the blank will be less than the WCL) would be greater than 99 %. To be most useful, this property must be demonstrated for the particular matrix being used, and not just for reagent-grade water.

5.2.5 Low Probability of False Non-detection—Where appropriate data have been used for calculations, the WDE provides a true concentration at which there is a high estimated probability (at least 95 %) of true detection (and thus a low estimated probability of false non-detection (β) equal to 5 % at the WDE), with a simultaneously low estimated probability of false detection. Thus, when a sample with a true concentration at the WDE is measured, the probability of detection would be estimated to be at least 95 %. To be useful, this property must be demonstrated for the particular matrix being used, and not just for reagent-grade water.

NOTE 1—The referenced probabilities, α and β , are key parameters for risk-based assessment of a detection limit.

5.3 When this practice is utilized by a laboratory to develop these false-positive- and false-negative-control point estimates, from data representative of routine operations, the laboratory may confidently claim these levels of false-positive and false-negative control in the future, so long as the data used remain representative of that future operation. The laboratory may also qualify reported data using the appropriate point estimates (for example YC, YD, WCL, WDE) or censor data below the WCL as a valid basis for these data-reporting practices.

5.3.1 The WDE Standard does not provide the basis for any prospective use of the test method by other laboratories for reliable detection of low-level concentrations, even for the same analyte and same media (matrix).

5.3.2 The WDE values from a given laboratory may be used to compare the detection power of different methods for analysis of the same analyte in the same matrix by that laboratory.

5.4 The WDE practice applies to measurement methods for which calibration error (that is, the error in the calibration of the measurement system) is minor relative to the combined other sources of variability. Some examples of other sources and when they may be dominant are:

5.4.1 Sample preparation (dominant especially when calibration standards do not go through sample-preparation steps).

5.4.2 Differences in analysts where a laboratory has more than one person who may perform each method step.

5.4.3 Instrument differences (measurement equipment), which could take the form of differences in manufacturer, model, hardware, electronics, separation columns, sampling rate, chemical-processing rate, integration time, software algorithms, internal-signal processing and thresholds, effective sample volume, and contamination level.

5.5 Reducing calibration error by use of allowable, though more stringent, calibration procedures (for example, multiple concentrations, replication, tight calibration-acceptance criteria, etc.) and through calibration verification (for example, analysis of a traceable standard from a second, independent source, calibration diagnostics) can reduce the magnitude of the calibration error.

5.6 Alternative Data-Quality Objectives—Other values for α , β , confidence, etc. may be chosen as parameters; however, this procedure addresses only those stated here in.

5.7 Collectively, the many sources of variation combine to cause within-laboratory measurements at any true concentration to be normally distributed. The assumption of normality is important for some of the statistics used; data normality should be assessed if there is reason to believe this assumption is not valid.

5.8 If control of false negatives is not a data-quality objective, the WCL determined through this procedure provides a sound criterion for future determination of false-positive control; in such cases, the laboratory may confidently claim that true values above the WCL have a statistically significant difference from like-matrix zero-concentration samples (for example, from the method blank), but nothing more.

5.9 Where as-measured values (for example, not corrected for bias), not true values are of interest, YC and YD may be used as these as-measured levels of the WCL and WDE.

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 Critical Value and Detection Estimate.

6.2 Development of Data for Input to the Calculations—A single WDE calculation is performed per analyte, matrix/media, and method. A minimum of five concentrations must be used to allow for high-quality estimation of true versus measured concentration, and for modeling the relationship of standard deviation to true concentration. A minimum of six values at each concentration are required in this practice to provide a high-quality estimation of the standard-deviation and the recovery relationships. Additional concentrations (and especially additional, representative, independent samples at each concentration) are highly encouraged, as they will reduce the uncertainty in the estimate. Data for each WDE 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.

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

- (1) Concentrations of available data, such as routine quality-control samples.
- (2) Potential use of the same data to calculate quantitation limits and or other control limits.
- (3) The anticipated or previously determined WDE (top of the range should exceed this value by at least a factor of 2).
- (4) The potential need to eliminate the lowest concentration(s) selected (see zero-concentration discussion above).

6.2.1.1 Where possible, select a WDE study design that has enough distinct concentrations to assess statistical lack of fit of the models (see Draper and Smith (3)). Recommended designs are: (a) The semi-geometric design at five or more true concentrations, T_1 , T_2 , and so forth, such as: 0, WDE_0/D^2 , WDE_0/D , WDE_0 , $D \times WDE_0$, $D^2 \times WDE_0$, where D is a number greater or equal to 2 and WDE_0 is an initial estimate of the WDE, (b) equi-spaced design: 0, $WDE_0/2$, WDE_0 , $(3/2) \times WDE_0$, $2 \times WDE_0$, $(5/2) \times WDE_0$. Other designs with at least five concentrations should be adequate, provided that the candidate design includes blanks, at least one concentration approximately equal to $2 \times WDE_0$, and at least one nonzero concentration below WDE_0 .

6.2.2 *Considerations for All True Concentration Selections:*

6.2.2.1 The range of the data should allow for a single model (ideally a straight-line model) in true concentration for mean recovery from zero to the maximum concentration in the study; also, a single model (one of the four models in this practice) in true concentration should describe the within-laboratory measurement standard deviation in the range from zero to the maximum concentration.

6.2.2.2 The concentration range must be sufficient to enable statistically significant coefficients to be estimated for the ILSD and mean-recovery models. The anticipated form of the ILSD model (that is, the relationship between within-laboratory measurement standard deviation and true concentration), if known, can help in choosing a WDE study design. Four ILSD models are provided herein: constant, straight-line (increasing), exponential (increasing), and hybrid. Chemistry, physics, empirical evidence, or informed judgment may make one model more likely than others. Evaluation of multi-laboratory method-validation studies (such as those produced by ASTM and EPA) may also provide valuable information.

6.2.2.3 The use of very high concentration data, outside of the trace range, should be minimized, as such data are more likely to be subject to a different modeling fit (as in flattening response at high concentrations) and will influence the WDE/WCL determinations. The user manual for DQCALC software provides instructions for evaluation of the software-generated graphics, which aid in identifying inappropriate high concentrations. General considerations include:

- (1) For methods where instruments are calibrated over a broad range (for example, multiple orders of magnitude), the concentrations selected for the study should never exceed the range in which linearity of calibration from the lowest calibration concentration has been demonstrated.

- (2) Where on-going quality-control 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.

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

NOTE 2—33%RSD approximates the 99 % confidence of three standard deviations and is a general approximation of the concentrations at which detection occurs.

NOTE 3—Where more than five concentrations are available, calculations with and without the highest concentration(s) included can also provide insight into the degree of impact the high concentration(s) is having on the recovery relationship and on the modeling of standard deviation.

6.2.2.4 To be used in the study, known, routine sources of measurement variability (consistent with those of routine analysis of samples) must be in action at the time of the generation of the data, if the WDE and WCL are to be used for characterizing routine performance. That is, in order for the WDE to represent routinely achieved detection, the data used for WDE calculation must be generated under routine analytical conditions at trace concentrations. Representative within-laboratory variation can only be seen if the number of qualified analysts and qualified measurement systems in the laboratory are represented. The more data used and the more combinations included, the less effect any specific bias in these pairings should have on the WDE estimate. Similarly, sample management (for example, holding time) and allowed variations in sample-processing procedures must be included. The time period spanned must allow for incorporation of routine sources of variation. 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 detection limits has been a primary component of poor-quality detection estimates and should be strictly avoided (garbage in, garbage out). Ideally, each measurement would be an unsuspected blind measurement made by a different analyst using a different (qualified) measurement system (that is, instrument) on a different day, in random order. In any case, the goal is to minimize special treatment of the study samples.

6.2.2.5 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 WDE. Where the end use is unknown, the data generator who is using it needs to disclose the specific attributes of the data used in the calculation (as well as the %RSD), and thus of the WDE.

6.2.2.6 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.

6.2.2.7 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.

6.2.2.8 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 software settings may 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; the presence of these processes as well as the setting of any operator-controllable setting should be evaluated.

NOTE 4—Qualitative criteria used by the method to identify and discriminate 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.

6.2.3.2 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 (see 6.2.3), 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).

6.2.3.3 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 and there must be at least six such data points. 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.

6.2.3.4 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 part of 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 the following against the quality of the zero-concentration data: 1) the number of other concentrations available, 2) the range of the other concentrations, and 3) the risk of extrapolation of the WDE outside the data-set concentration range.

6.2.3.5 *True Concentrations Near Zero*—As with concentration zero, true concentrations very near to zero may also have been censored, have been 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 the Relationship between Standard Deviation and 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 WDEs.

NOTE 5—See Caulcutt and Boddy (4) 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 (5) for further discussion of standard-deviation modeling. The model order is as follows:

Model A (Constant ILSD Model):

$$s = g + \text{error} \quad (1)$$

where: g is 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):

$$s = g + h \times T + \text{error} \quad (2)$$

where: g and h are 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):

$$s = \{g^2 + (h \times T)^2\}^{1/2} + \text{error} \quad (3)$$

where: g and h are fitted constants. Under Model C, 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):

$$s = g \times \exp\{h \times T\} + \text{error} \quad (4)$$

where: g and h are 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.

6.4.2 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.

6.4.3 Practice D7510, describes the DQCALC software that performs the calculations for each of the four models, as well as the fit of each. The software identifies which model produced the best fit, and allows the user to select this model or to select 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(s) for the choice should be scientific and should be recorded to document the WQE.

6.4.4 Users of this practice not using the ASTM D19 DQCALC software will find a procedure 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 regression 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 6—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,

Model R:

$$Y = a + b T + \text{error} \quad (5)$$

6.5.2 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 2, or Caulcutt and Boddy (4)). If a non-constant standard-deviation model was selected, then WLS should be used to fit mean recovery; then, the estimates of the coefficients (a and b) will be approximately the minimum-variance unbiased linear estimates. The WLS procedure is described in the IDE standard, Practice D6091.

6.6 *Determine the Critical Value and from it the Detection Estimate Value*—By means of the recovery curve and the most

appropriate model of standard deviation to true concentration, the level of false-positive control is first established.

6.6.1 YC is determined as the minimum concentration at which the false positive rate of 1 % (with confidence based on sample size and tolerance interval; for example, 90 % coverage) is achieved. See Fig. 1 and Fig. 2. Alternative criteria for false-positive rate and “coverage” by the tolerance interval may also be used, based on alternative data-quality objectives.

6.6.2 It can be seen from the graphical representation that includes the recovery relationship, Fig. 2, that the critical value (where there is 99 % control of false-positive values at true-concentration zero) is the point at which measured concentration, YC, intersects the recovery curve. Consequently, WCL (which is in true concentration units) is established. The modeled standard deviation at true concentration zero (along with the tolerance interval for 90 % based on the sample size) are the estimates used to establish YC. WCL is the true concentration equivalent to YC, as established by the recovery curve. In Fig. 2, the example demonstrates a case with positive bias (intercept greater than zero) and imperfect recovery (slope of the calibration not equal to 1).

NOTE 7—This example highlights the advantages of the WDE procedure over more simplistic procedures. More simplistic procedures make often inappropriate assumptions about slope (that is, assumed to be 1) and y-intercept (that is, assumed to be zero at true-concentration zero), in addition to assuming that the standard deviation is constant. Additionally, where the simplest model (constant) for standard deviation is rejected, this WDE procedure requires that weighted least squares be used for the recovery curve, to prevent the higher concentrations from having an excessive effect on the fitting of the line; most other practices do not include this requirement.

6.6.3 Figure 2 also shows a horizontal line drawn from YC, parallel to the x -axis and intersecting a bell-shaped curve. This line is equivalent to the point LC in Fig. 1 and demonstrates the relationship of these two figures. (Figure 2 incorporates the complexity of the recovery relationship, while Fig. 1 does not. The WDE is then the 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), there is control of false negatives to, on average, 5 %. Alternative criteria for false-positive rate and “coverage” by the tolerance interval may also be selected, based on alternative data-quality objectives.

NOTE 8—The ordinate value for WDE (that is, YD) could also be established, were YD of interest to the user.

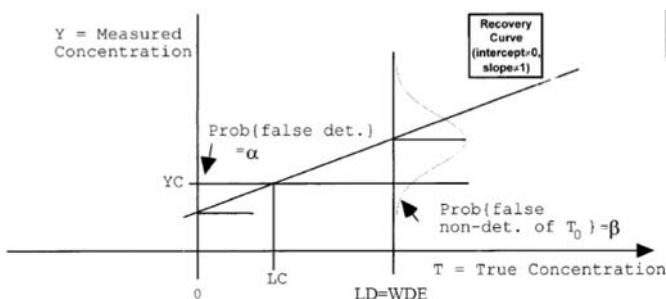


FIG. 2 Critical Level and Detection Estimate—Incorporating Concepts of Figure 1 with the Recovery Relationship

6.7 An example (with data, calculations and graphical representations) is provided in Appendix X1.

7. Review, Documentation, and Reporting

7.1 The WDE analysis report should include the identification of laboratory, 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 (that is, statistical) analysis should be included or referenced (for example, the output file from the DQCALC software) and the calculated WDE values recorded. Also, the standard-deviation model selected, and the coefficient estimates for this model and for the mean-recovery model should be reported. Where a statistical model other than the mathematical best fit has been chosen, the reasoning should be described.

8. Report

8.1 The analysis report should, at a minimum, 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,
- 8.1.11 Coefficient estimates for the ILSD model and for the mean-recovery model.

NOTE 9—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 practice 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.

9. Rationale

9.1 The basic rationale for the 99 %/95 % WDE is contained in Currie (1), and is shown in Fig. 1. For a selected test method, this figure shows single-laboratory variation in measurements of both blank samples and samples at true concentration = T_0 , assuming perfect recovery. The variation shown is according to the Normal distribution, with known mean, insignificant bias, and known within-laboratory standard deviation. The critical value, LC^* , is used to determine detection. LC^* can be moved to decrease α (which is the probability of a false detection), but at the price of increasing β (which is the probability of a false non-detection); the reverse can also be done. Given an acceptable value for α , a value for LC^* can be found. Given, also, an acceptable value for β , a suitable value for T_0 can be found. T_0 is then a single-laboratory detection limit, at which reliable detection can occur by definition of acceptable α and β . By following this WDE procedure, these concepts (that is, LC^* and LD) can be implemented in a scientifically rigorous manner to produce within-laboratory detection-capability estimates.

9.2 There are several complications to Currie's theory (and Fig. 1) in application to real-world analytical testing. See Maddalone et. al. (7) and see Gibbons (8). Listed below are common and significant complications, along with remedies that are provided through use of this practice and development of WDE/WCLs:

9.2.1 Recovery is rarely perfect. The relationship between measured values and true concentrations cannot be assumed to be trivial and needs to be assessed. Where there is a difference between true and measured values, the difference can and should be modeled, typically by a straight line. This WDE standard performs this activity; the DQCALC software provides coefficients and plots of residuals for user assessment. The WDE and WCL account for this recovery and are reported in units of true concentration. Where recovery is perfect, measured (YC and YD) and true (WCL and WDE, respectively) will coincide.

9.2.2 Variation can be introduced by different analysts, models, instruments, environmental factors, latitude in a test method, contamination, carry-over, and other factors. Data collected at only one point in time (or over a period of time insufficient to encounter these factors) will under-represent variability. The collective contributions to measurement within-laboratory standard deviation can be observed in the data, if such contributions are included in the method processes and are allowed to vary during the data-collection time. This practice provides specific guidance regarding the representativeness of data used to calculate the WDE.

9.2.3 The within-laboratory standard deviation of measurements is an unknown in nearly all testing procedures. Standard deviations must be estimated with finite sample sizes, and statistical tolerance limits must be used to obtain high (stated) confidence in a distribution-quantile estimate. Most existing procedures (and all procedures that utilize confidence intervals) do not address this issue. This practice provides for 90 % confidence, using the appropriate tolerance (k) factor. The greater the quantity of data used in the estimate, the less uncertain the standard deviation (and the lower the tolerance k factor). This practice's requirement for quantity of data was developed by consensus and represents the minimum the task group found to be advisable. Increasing the size of n is highly recommended in this practice.

9.2.4 Within-laboratory standard deviation of measurements may change with true concentration, possibly due to underlying physical principles of the test method, or measurement system (for example, detector), or both. The simplifying assumption that standard deviation is constant (or that the change is insignificant) has been found to be a poor assumption in many cases, especially at trace levels, and has been a primary motivation for development of this practice. Also, the assumption that there is a linear relationship of standard deviation to concentration frequently has been found to be a poor assumption, although better than assuming constant standard deviation when variation does exist. Nevertheless, if the straight-line model is an inadequate fit, the critical-level and detection estimates can be affected adversely. In the WDE procedures, the inclusion of non-linear models (exponential and hybrid), and the evaluation of the fit of the models relative to the constant and linear models, is specifically to address this failing.

9.2.5 If standard deviation is not constant, the use of ordinary least squares is suspect and will adversely affect any determinations. This fact is particularly important for detection estimation, because the modeling of the recovery data (true versus measured) at the lowest concentrations is critical. Many procedures do not take recovery bias (true versus measured) into account at all. This failing is serious in many situations. This practice not only assesses measured-versus-true concentration, but also assesses standard deviation; where an assumption of constant standard deviation is not adequate, this practice uses weighted least squares to fit a linear model to the recovery data (and thereby better estimate and correct the bias at the lower concentrations).

10. Keywords

10.1 critical limit; detection; detection limit; false detection; false non-detection; false positive; matrix effects; statistical tolerance interval; true detection; true non-detection

APPENDIX

(Nonmandatory Information)

X1. EXAMPLE (STRAIGHT-LINE ILSD MODEL)

TABLE X1.1 Computations to Estimate Straight-Line Model Coefficients by Means of Least Squares—Ordinary and Weighted

Ordinary Least Squares, OLS	Weighted Least Squares, WLS
$\bar{T} = \frac{1}{n} \sum_{i=1}^n T_i$	$\bar{T}_w = \frac{\sum_{i=1}^n W_i T_i}{\sum_{i=1}^n W_i}$
$\bar{y} = \frac{1}{n} \sum_{i=1}^n y_i$	$\bar{y}_w = \frac{\sum_{i=1}^n W_i y_i}{\sum_{i=1}^n W_i}$
$S_{TT} = \sum_{i=1}^n (T_i - \bar{T})^2$	$S_{wTT} = \sum_{i=1}^n W_i (T_i - \bar{T})^2$
$S_{TY} = \sum_{i=1}^n (T_i - \bar{T})(y_i - \bar{y})$	$S_{wTY} = \sum_{i=1}^n W_i (T_i - \bar{T})(y_i - \bar{y})$
$\text{Slope} = b = S_{TY}/S_{TT}$	$\text{Slope} = b = S_{wTY}/S_{wTT}$
$\text{Intercept} = a = \bar{y} - b\bar{T}$	$\text{Intercept} = a = \bar{y}_w - b\bar{T}_w$

X1.1 Identify and Fit the ILSD Model—Ten combinations of analysts and instruments were involved in a WDE study where single measurements were made at each of five concentrations, including blanks: $T_k = 0, 0.25, 0.50, 1, 2$ ppb.

NOTE X1.1—Considerations prior to calculations are not addressed in this example.

X1.1.1 The reported measurements are shown in Table X1.3. These values are also shown in Fig. X1.1. The straight-line recovery model appears to be plausible, and the data appear to have within-laboratory measurement standard deviation that increases with concentration. Note that for this

example, high blank measurements and an unusually high recovery slope are present.

X1.1.2 Within-laboratory sample standard deviations at each true concentration are computed, and are shown in Table X1.3.

X1.1.3 A plot of within-laboratory sample standard deviation versus true concentration is shown in Fig. X1.2. There is increasing qualitative evidence of an increase in standard deviation with increasing concentration.

X1.1.4 A straight-line regression (OLS) is conducted of the within-laboratory sample standard deviations, s_k , versus T_k . The results are shown in Table X1.4, and the fit is shown in Fig. X1.2. The estimates are intercept $g = 1.0891$ and slope $h = 0.95682$.

X1.1.5 The p -value associated with the slope estimate, h , is $1.28\% < 5\%$, so Model A, the constant ILSD model, is rejected.

X1.1.6 The residuals from the straight-line within-laboratory standard deviation fit are computed as follows and are displayed in Fig. X1.3:

$$r_k = s_k - (1.089 + 0.957 \times T_k) \quad (\text{X1.1})$$

X1.1.7 There is no evidence of systematic curvature, so the analysis proceeds to the next step of the practice.

X1.2 Fit the Mean Recovery Model

X1.2.1 Since the within-laboratory standard deviation has been shown to be nonconstant with respect to true concentration, WLS is used to fit the mean recovery model, and the fitted ILSD model is used explicitly to estimate the ILSD at arbitrary true concentrations.

TABLE X1.2 90 %-Confidence Upper, One-sided Statistical Tolerance Limit Factors for Computing the 99 %/95 % WDE^A

Number of Observations Retained, n	99 % Quantile, k_1	95 % Quantile, k_2
5	4.67	3.40
10	3.53	2.57
15	3.21	2.33
20	3.05	2.21
25	2.95	2.13
30	2.88	2.08
35	2.83	2.04
40	2.79	2.01
45	2.76	1.99
50	2.74	1.97
55	2.71	1.95
60	2.69	1.93
65	2.68	1.92
70	2.66	1.91
75	2.65	1.90
80	2.64	1.89
90	2.62	1.87
100	2.60	1.86
150	2.55	1.82
200	2.51	1.79

^AComputed using STINT software (93/12/3 version), by Prof. W. Meeker and J. Chow of Iowa State University.

TABLE X1.3 Reported Measurements and Computed Statistics from WDE Study

True Concentration T_k , ppb	Reported Measurement, Y_i (ppb), one per Analyst-Instrument combination	Sample Standard Deviation	Predicted Standard Deviation	Weights for WLS
0.0	1.41, 3.94, 2.22, 3.48, 1.96, 0.92, 2.17, 2.36, 4.50, 3.26	1.137	1.089	0.843
0.25	4.10, 3.51, 4.07, 4.34, 4.54, 2.76, 2.03, 4.13, 6.06, 6.47	1.336	1.328	0.567
0.50	3.97, 7.34, 6.41, 6.25, 6.38, 7.64, 4.67, 6.74, 4.38, 6.48	1.255	1.568	0.407
1.0	7.54, 7.68, 8.38, 7.14, 3.12, 10.97, 11.15, 10.44, 9.73, 7.27	2.406	2.046	0.239
2.0	8.20, 13.97, 12.88, 18.31, 16.47, 16.06, 12.56, 14.21, 13.96, 17.37	2.900	3.003	0.111

TABLE X1.4 Results of Straight-Line Fit of s_k versus T_k by OLS

Linear Fit				
Standard Deviation (Y) = 1.0891 + 0.95682 T				
Standard Deviation (Y) = g + h T				
Summary of Fit				
RSquare			0.904996	
RSquare Adj			0.873329	
Analysis of Variance				
Source	df	Sum of Squares	Mean Square	F Ratio
Model	1	2.2887587	2.28876	28.5778
Linear Fit				
Error	3	0.2402664	0.08009	Prob>F
C total	4	2.5290251		0.0128
Parameter Estimates				
Term	Estimate	Standard Error	T-Ratio	Prob> T
g (intercept)	1.0891019	0.184493	5.90	0.0097
h (slope)	0.9568195	0.178985	5.35	0.0128

TABLE X1.5 Results of WLS Fit of Straight-line Mean Recovery Relationship (Measured Concentration versus True Concentration)

Response: Y-Linear Fit				
Y = 2.729549 + 5.8711952 T				
Y = a + b T				
Summary of Fit				
RSquare		0.794662		
RSquare Adj		0.790384		
Root Mean Square Error		0.982227		
Lack of Fit				
Source	df	Sum of Squares	Mean Square	F Ratio
Response: Y-Linear Fit				
Lack of fit	3		0.26311	0.2601
		0.789330		
Pure error	45	45.519596	1.01155	Prob>F
Total error	48	46.308925		0.8537
Parameter Estimates				
Term	Estimate	Standard Error	T Ratio	Prob> T
a (intercept)	2.729549	0.264938	10.30	<0.0001
b (slope)		5.8711952	0.430774	13.63
				<0.0001
Analysis of Variance				
Source	df	Sum of Squares	Mean Square	F Ratio
Model	1	179.21612	179.216	185.7606
Error	48	46.30893	0.965	Prob>F
C total	49	225.52504		<0.0001

The estimate of intercept, g , and the estimate of slope, h , in the straight-line ILSD model, are used to predict the ILSD at each true concentration, T_k . These predicted values, s_k' , are shown in [Table X1.3](#) and are assumed to be closer to the true ILSDs, s_k , than are the sample ILSDs, s_k .

X1.2.2 Weights are computed, based on the predicted ILSDs:

$$w_k = (s_k')^{-2} \quad (\text{X1.2})$$

They are shown in [Table X1.3](#).

X1.2.3 The WLS is carried out to estimate the coefficients, a and b , of the straight-line mean recovery relationship:

Model R:

$$Y = a + b \times T + \text{error} \quad (\text{X1.3})$$

The results of WLS are shown in [Fig. X1.4](#) and in [Table X1.5](#).

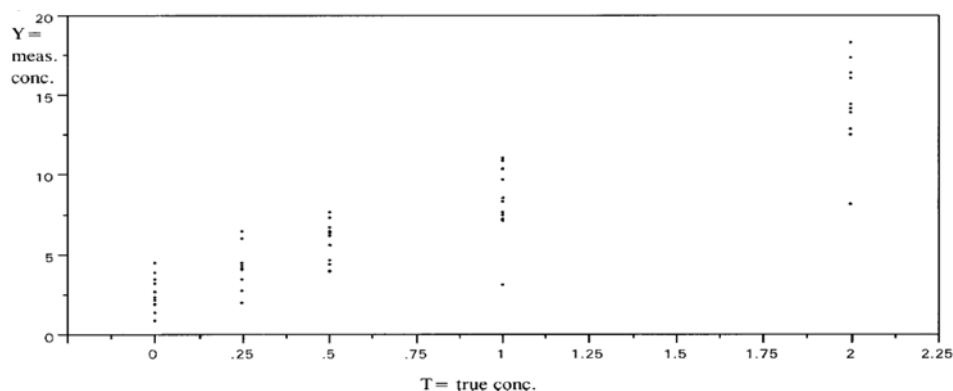


FIG. X1.1 Reported Measurements versus True Concentration, One Measurement/Analyst-Instrument Combination at Each Concentration (ppb)

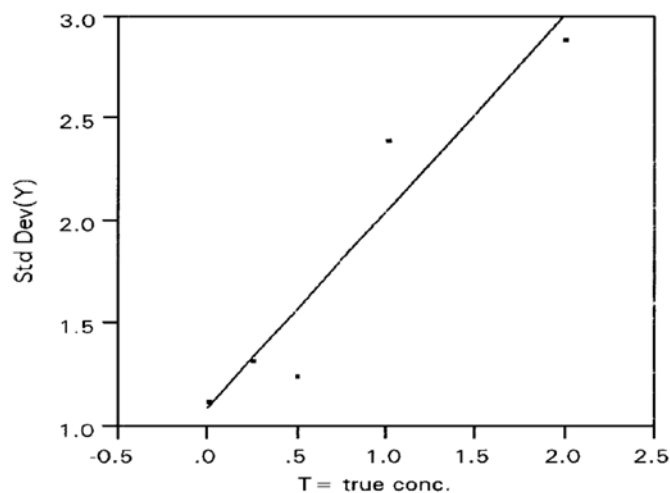


FIG. X1.2 Sample Standard Deviation (Y) versus True Concentration (s_k versus T_k)

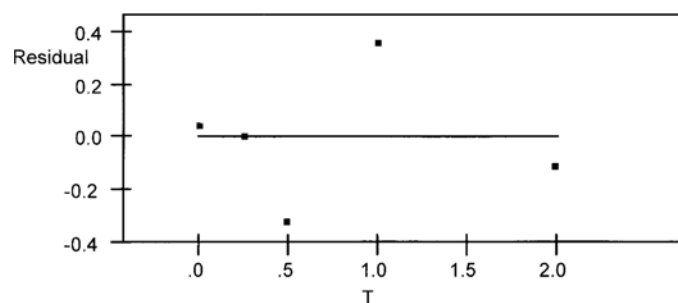


FIG. X1.3 Residuals from Straight-Line Model of Within-laboratory Measurement Standard Deviation versus True Concentration

X1.2.4 The fit is evaluated as follows: (1) The overall p -value is $<0.0001 < 5\%$; (2) The lack of fit p -value is $0.8537 > 5\%$; (3) Fig. X1.5 shows a plot of the residuals versus true concentration and shows no evidence of systematic curvature. Therefore, the straight-line mean recovery fit is acceptable.

X1.3 Compute the WDE

X1.3.1 Having obtained acceptable fits of a ILSD model and a mean recovery model, the WDE can be computed.

X1.3.2 The recovery critical value, YC , is computed and is shown in Fig. X1.4:

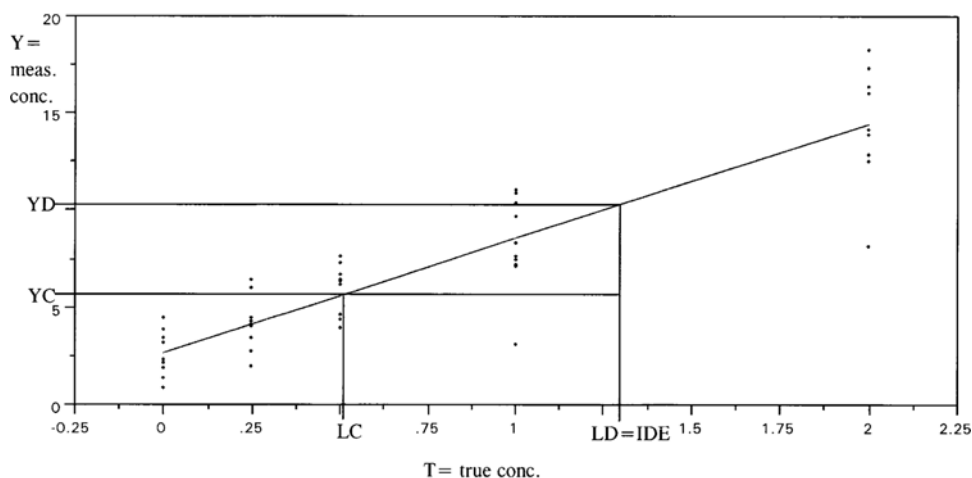


FIG. X1.4 Weighted Least Squares Fit of Mean Recovery Relationship, with WDE and Critical Limits

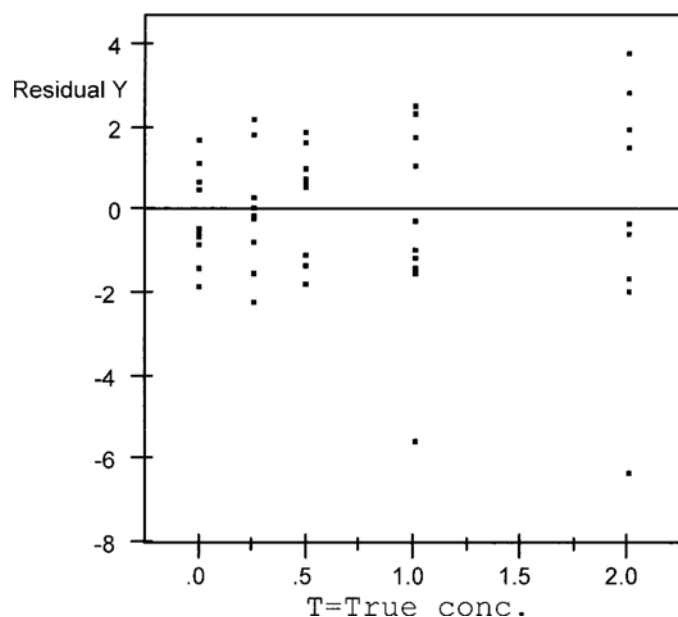


FIG. X1.5 Plot of Residuals from WLS Fit of Straight-line Mean Recovery Relationship versus True Concentration

$$YC = k1 \times \hat{s}(0) + a = 2.74 \times 1.089 + 2.73 = 5.71 \quad (\text{X1.4})$$

where:

$k1 = 2.74$ = the one-sided statistical tolerance limit for 90 % confidence of the 99 % quantile, based on the normal distribution assumption and $n=50$ observations,

$s_0 = g = 1.089$ is the predicted ILSD at $T=0$ (blank samples), and

$a = 2.73$ = intercept from the mean recovery curve (recall that this is set much higher than 0 for this example to clearly distinguish measured values from true values in the plots and tables, see 10.1.1)

X1.3.3 The true concentration critical value is computed and is shown in Fig. X1.4:

$$LC = (YC - a)/b = (5.71 - 2.73)/5.87 = 0.51 \text{ ppb } LC = WCL \quad (\text{X1.5})$$

where:

$b = 5.87$ = slope of the recovery curve

X1.3.4 The WDE (also called the LD , in the tradition of Currie (1)) is computed recursively. An initial value is set as follows:

$$LD_0 = LC + k2 \times \hat{s}(0)/b = 0.51 + 1.97 \times 1.089/5.87 = 0.874 \quad (\text{X1.6})$$

where:

$k2 = 1.97$ = one-sided statistical tolerance interval for 90 % confidence of the 95 % quantile, based on the normal distribution assumption and $n=50$ observations

Then the recursive function is solved, iteratively, as follows:

$$LD_1 = R^{-1} \left(k1 \times \hat{s}(0) + k2 \times G(LD_0) + a \right) = LC + k2 \times (g + h \times LD_0)/b = 0.511 + 1.97 \times (1.089 + 0.957 \times 0.874)/5.87 = 1.154 \quad (\text{X1.7})$$

$$LD_2 = 0.511 + 1.97 \times (1.089 + 0.957 \times 1.154) / 5.87 = 1.245 \quad (\text{X1.8})$$

etc., until convergence is achieved at about the eighth iteration, $LD_7 \approx LD_8 = 1.287$. Therefore, $WDE = LD = 1.287 \approx 1.3$ ppb, as is shown in Fig. X1.5. Note that $LD > 2 \times LC = 1.02$.

X1.4 Based on the data input, there is (approximately) 90 % confidence that the analyte can be detected at least 95 % of the time at 1.3 ppb, and simultaneously that blank samples will

result in non-detect no more than 1 % of the time.

NOTE X1.2—In this example the calculated WDE is less than most calculated standard deviation values in Table X1.3. This is because the data used in this example reflect high blank values and an unusually high recovery slope. This example serves to illustrate the utility of the practice for less than ideal situations.

X1.4.1 Also shown in Fig. X1.4 is the expected measurement value at the WDE concentration:

$$YD = R(LD) = a + b \times LD = 2.73 + 5.87 \times 1.287 = 10.3 (\text{X1.9})$$

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