Designation: D7729 – 12

Standard Practice for Determining and Expressing Precision of Measurement Results, in the Analysis of Water, as Relative Standard Deviation, Utilizing DQCALC Software[1]

This standard is issued under the fixed designation D7729; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This Practice describes a procedure for developing a graphical model of relative standard deviation vs concentration for a analytical methods used in the analysis of water (methods that are subject to non-additive random errors) for the purpose of assigning a statement of noise or randomness to analytical results (commonly referred to as a precision statement), in either a manual or an automated fashion.

1.2 Data analysis and modeling is done with D19 Adjunct DQCALC (an Excel based tool).

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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

2. Introduction

2.1 An understanding of the uncertainty associated with measurement results is necessary for evaluating the utility of those results. Without a reported uncertainty estimate, users of measurement results are unable to determine if the data are sufficiently precise for any specific data use.

2.2 Measurement Uncertainty is most generally understood to be "a parameter characterizing the dispersion of the quantity values being attributed to a measurand" (from International Vocabulary of Metrology (VIM) 2.26). This definition can be implemented as an expression ("uncertainty statement") associated with an reported measurement that represents the statistically based (Type A estimate) dispersion of experimental results around a reported value.

2.3 There is no universally agreed upon format or nomenclature for uncertainty statements. The literature offers suggestions ranging from simple expressions of standard deviation or "fractional uncertainty" (standard deviation divided by reported result) to confidence intervals to detailed "uncertainty reports".

2.4 In addition to the "random" errors encompassed in the ideas expressed in 1.1 and 1.2, above, there are also "systematic" errors, biases, that can be considered as part of uncertainty. The literature is not consistent on how unknown bias is considered in an uncertainty statement. For purposes of this Standard, bias is assumed to have been corrected for or insignificant in the reported results, and bias is not specifically incorporated in the proposed uncertainty statement.

2.5 For purposes of this Standard, the terms "MU", uncertainty statement, or measurement uncertainty will be used synonymously to designate the expression accompanying measurement results for the purpose of assessing the utility of those results.

2.6 This Standard proposes the use of fractional uncertainty or Relative Standard Deviation (RSD) as the expression of MU.

2.7 Traditionally, in the generation and publication of data related to the analysis of water, a continuous function (model) describing the relationship of uncertainty (as standard deviation) to concentration is not available. To compensate for this lack, discrete points bounding certain levels of uncertainty are calculated, for example, "detection limits" (typically around 33% RSD) and "quantitation limits" (often around 10% RSD). Results are flagged to indicate their relationship to one of these limits. Alternatively, this Practice directs the creation of a model of uncertainty (RSD vs concentration) which allows assignment of a discrete uncertainty estimate to any result value measured within the range of modeled data.

2.8 This Practice is based on the use of the DQCALC software that was developed to simplify the calculation of the IQE – Inter-laboratory Quantitation Estimate (D6512). This Practice is restricted to the development of an uncertainty model for the reporting of MU within a single laboratory. In

[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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addition to providing an estimate of single-laboratory measurement uncertainty, the DQCALC software automatically calculates LC – from Curie, equivalent to EPA's MDL, and the ASTM Detection Estimate for a single lab (this utilizes a "3 sigma" tolerance interval rather than the standard confidence interval).

2.9 This Practice provides the tools to allow a Laboratory to embed the RSD vs Concentration relationship into a sufficiently powerful Laboratory Information Management System (LIMS) resulting in the ability to automatically report MU with all data reported out of the LIMS for modeled parameters.

2.10 The DQCALC Software is available from ASTM (see Standard D7510).

2.11 In addition, this Standard discusses the variables that should be considered for inclusion in the uncertainty modeling study.

3. Referenced Documents

3.1 *ASTM Standards:*[2]

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

3.2 *Other Standard:*[3]

International Vocabulary of Metrology Basic and General Concepts and Associated Terms, VIM, 3rd edition, JCGM 200:2008

4. Terminology

4.1 *Definitions:*

4.1.1 *Measurement Uncertainty, n*—in the analysis of water, a value representing the precision of a reported determination.

4.1.2 in the analysis of water, a value representing the precision of a reported determination, expressed as the relative standard deviation of typical measurements of the same form.

4.2 *Symbols*

IQE – Inter-laboratory Quantitation Estimate
LIMS – Laboratory Information Management System
MU – Measurement Uncertainty
RSD – Relative Standard Deviation

5. Summary of Practice

5.1 The relationship between Relative Standard Deviation and concentration is modeled using a multi-replicate and multi-level design and utilizing the curve fitting tools in the DQCALC software. The DQCALC software will return the coefficients for the selected function/model of standard deviation against concentration. The general equations are given in this Practice. From the equation, the appropriate standard deviation for any concentration in the range represented in the model study can be calculated. This can then be converted into RSD, the recommended reporting format.

5.2 The IQE Practice that forms the basis for this Practice, has the feature of correcting for recovery. Therefore, for purposes of this Practice true concentrations, that is, concentrations that have been "corrected" for recovery bias are used. Where a laboratory in use of its methods of testing does not correct resultant values, the calculated RSD will be marginally higher or lower, depending on the magnitude of the uncorrected bias in the reported data. Where uncorrected bias is less than 10% of the magnitude of the result, the error in the RSD estimate may be considered insignificant.

6. Sources of Imprecision

6.1 When utilizing the result of a measurement to make a binary decision (yes/no, pass/fail, etc.) there is a risk of making a false positive determination (saying a condition exists when it does not) or a false negative determination (saying a condition does not exist when it does). The more precise the estimate of the measurement uncertainty of the result (the smaller the relative standard deviation), the less chance there is of making such incorrect assessments.

6.2 The most precise possible estimate of a result's MU would be obtained through replicate measurements done at the same time as the initial measurement. (This would, of course, also give a more precise estimate of the measurement result – a mean with n >1). The greater the number of replicates performed, the better the estimate of MU. In practice, this level of analytical work is rarely performed, unless there are dire consequences associated with the result.

6.3 Under typical circumstances in analytical laboratories, uncertainty is not determined from replicates of real-world samples. An assumption (rarely tested) is made that the uncertainty of the measurements of standards of known (traceable) concentration is comparable to the uncertainty of measurements on real world samples. It is well known that different matrices, especially matrices with suspended matter containing the analyte, have much different measurement uncertainties and they are typically greater than that of measurements on traceable standard solutions, but for pragmatic reasons this is often ignored. This means uncertainty estimates determined from standards run in replicate with the real world sample measurement, are estimates of uncertainty that are typically much smaller (implying much better precision) than is warranted and are estimates of the method performance on ideal samples.

6.4 But, again, under typical circumstances, replicate standard determinations are not performed with each particular real world sample measurement. They are typically performed across different batches, different days, different operators, and, even across different laboratories. Each of these elements or variables – batch, day, etc. – adds an extra component of "noise", each increasing the magnitude of the uncertainty estimate.

6.5 Within each prescribed set of variables (given batch, day, operator, etc.), the replicate precision obtained is often

[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] Available from BIMP at http://www.bipm.org.

comparable. But, due to varying "conditions" (usually unknown and undeterminable) the mean result under each condition differs. This difference between mean results under different conditions is what adds additional variability – extra noise – and increases the magnitude of the measurement uncertainty estimate. Essentially, as each new variable is added to the uncertainty determination, biases become incorporated as random noise.

6.6 The net result of these assumptions and non-ideal conditions of test during MU estimation is that the MU value obtained and reported is itself uncertain, and the magnitude of error in the MU estimate is difficult or impossible to determine.

6.7 As a matter of practicality, even with the use of standards rather than real-world sample replicates and the inclusion of "extra" sources of noise, the MU estimates obtain usually bear a useful relationship to the analytical results they are reported with, and provide a reasonable ballpark of uncertainty for the data users.

6.8 In utilizing this Practice to obtain MU estimates to be reported with real-world sample results, the user is cautioned to be cognizant of these caveats in choosing what sources of variability - temporal, procedural, material, etc. – are to be included in the MU study design. Users will need to recognize that estimates of MU that incorporate sources of variability inappropriate to the data use or exclude sources that are appropriate to the data use may produce uncertainties that are typically smaller than would be most appropriate to the data use.

7. Relative Standard Deviation vs. Concentration Models

7.1 As explained in D7512 (IQE), the D19 approach to establishing a relationship between standard deviation and concentration involves generating independent measurements at predetermined concentrations over the analytical range of interest, including down to zero concentration or the blank, where of interest.

7.2 The standard deviations (and means) from the independent measurements at each concentration are calculated. These results are corrected for bias. Four models of the function of standard deviation to true concentration are fitted. The model with the best fit is determined. The relationship of measured concentration to true concentration is established through linear regression. Least squares is used where the standard deviation model selected was any model other than constant, for the other three models, the linear regression of true vs measured concentration is established using weighted least squares.

7.3 The four models used for fitting standard deviation vs true concentration are : constant, exponential, straight-line, and hybrid. Multiple statistical tools and graphs are presented to help the user decide which model is the best fit.

7.4 It is the responsibility of the user to make the most appropriate choice between models. The simplest model that adequately represents the data over the range of interest for the intended use should be selected.

8. Procedure

8.1 Carry out a precision analysis study designed as described in D7512 (IQE). The study must have the following characteristics:

8.1.1 The study should have a minimum of 5 levels and 5 replicates at each level. More levels and more replicates produce better estimates. One of the levels must be in near or in the range of detection, with analysis of an uncensored blank ideal. Three of the levels should be at approximately 3, 7 and 10 standard deviations of the instrument noise. The remaining two should be at the mid-range and undiluted maximum of the analytical procedure. The goal is to best characterize the uncertainty (standard deviation) across the analytical range of the test method, with extra focus on the area of the relationship where there is the most change (typically between 10% and 30% relative standard deviation).

8.1.2 Determine which analytical variables are appropriate for inclusion in the study design.

8.1.3 Conduct the study and tabulate the results. Individual measurements must be evaluated and if determined to be erroneous should be eliminated using an accepted, scientifically-based reasoning. Identification of potential outlier 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.

8.2 Tabulate the results as instructed in D7512(IQE) in an Excel spreadsheet. For this practice, the columns for Lab and Batch will contain only "1's". The exact format for the headers in the table are critical or the DQCALC program will not complete the data import.

8.3 Import the data into DQCALC and complete the computation of the IQE, including outlier identification and removal and evaluation of the most appropriate model of standard deviation vs. true concentration. Note the initial n value, the final n value, specific outliers removed and the reason for any outlier removal as well as the SD model selected.

8.4 Extract the coefficients for the appropriate model's formula. The coefficients are found on the DQCALC tab titled "DL&QL".

9. Determination of Relative Standard Deviation for a given concentration

9.1 Insert the concentration (t) for which the RSD is desired into the model equation derived in 8.4, above to calculate the associated standard deviation (s). Calculate the RSD as: $RSD = (s/t) \times 100$

10. Reporting measurement uncertainty

10.1 Currently, there are no universally accepted protocols for the reporting of measurement uncertainty. In this Practice, it is recommended that Relative Standard Deviation be used as the parameter of choice for this expression. The rationale for this recommendation is that although standard deviation can be back calculated from %RSD, data quality concerns (detection, quantitation, etc.) are more easily and directly intuited from

TABLE 1 Model formulas

MODEL	Formula	Cell location for "g" (DL& QL Sheet)	Cell location for "h" (DL& QL Sheet)
Constant	$s = g$	B10	N/A
Straight line	$s = g + ht$	B13	B14
Hybrid	$s = (g^2 + [ht]^2)^{1/2}$	B21	B22
Exponential	$S = g\ (10^{(ht)})$	B17	B18

TABLE 1 Key

s	Sample standard deviation
t	Concentration (true; corrected for recovery)
g	Fitted constant ("intercept")
h	Fitted constant ("slope")

%RSD. For example, for 99% confidence of detection, one knows that %RSD must be below 33%.

10.2 Since the DQCALC software returns standard deviation values, and since most other MU reporting protocols start with standard deviation, this Practice can be used as the starting point for other MU reporting schemes.

10.3 To avoid potential misinterpretation, it is recommended that MU ("X") be reported as a parenthetical statement following the measurement value as ("X" % RSD, for example 20 mg/L (2.3 % RSD)).

10.4 Most Laboratory Information Management Systems provide capabilities to automate calculations and to provide for the reporting of MU with the reported result.

10.5 Example graph: Fig. 1 provides an example of the visual representation of the modeled RSD for a typical measurement (as displayed in DQCALC). Results for all of the models are displayed along with points where 10%, 20% and 30% IQE fall. The 30% IQE roughly equates to the Detection Estimate, and 10% RSD is a typically selected Quantitation Limit.

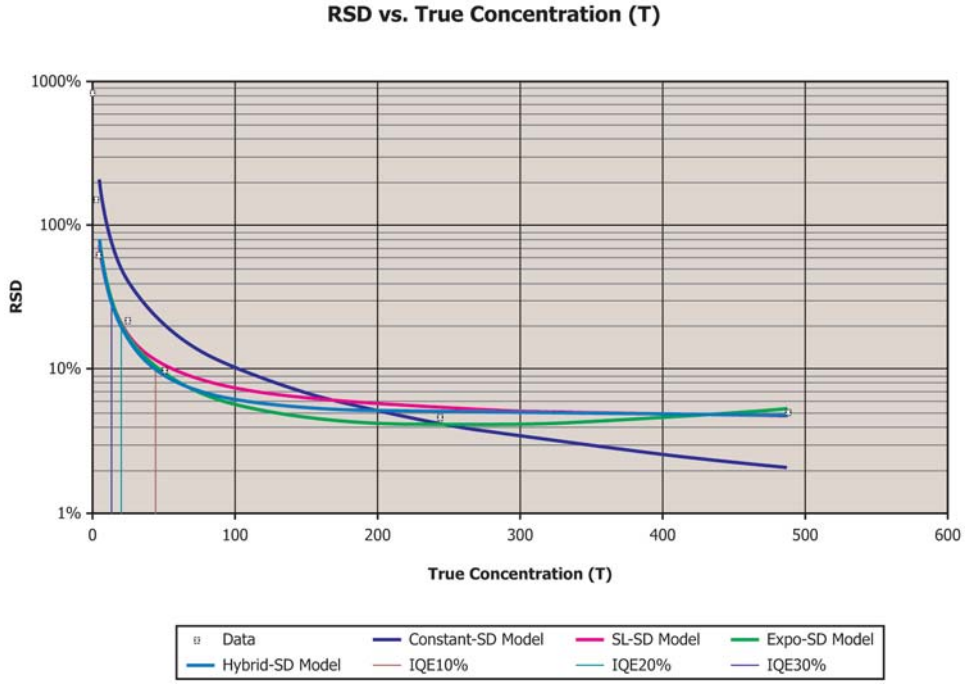

FIG. 1 RSD vs. True Concentration (T)