Designation: D7729 – 12 (Reapproved 2018)[ε1]

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.

ε[1] NOTE—The Keywords section was added editorially in August 2018.

1. Scope

1.1 This practice describes a procedure for developing a graphical model of relative standard deviation versus concentration for 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 Committee D19 Adjunct DQCALC[2] (a Microsoft Excel[3]-based tool).

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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 (MU) is most generally understood to be "a parameter characterizing the dispersion of the quantity values being attributed to a measurand" (from 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, 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 practice, 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 practice, 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 practice 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 %

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[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] Available from ASTM International Headquarters. Order Adjunct No. ADJDQCALC. Original adjunct produced in 2007.

[3] Microsoft Excel is a trademark of the Microsoft Corporation, Redmond, WA.

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 versus 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 inter-laboratory quantitation estimate (IQE) (Practice D6512). This practice is restricted to the development of an uncertainty model for the reporting of MU within a single laboratory. In addition to providing an estimate of single-laboratory measurement uncertainty, the DQCALC software automatically calculates L_C – from Curie, equivalent to the United States Environmental Protection Agency (EPA)'s method detection limit (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 versus 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 Practice D7510 and Adjunct DQCALC[2]).

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

3. Referenced Documents

3.1 *ASTM Standards:*[4]

D1129 Terminology Relating to Water

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 Documents:*[5]

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

4. Terminology

4.1 *Definitions:*

4.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

4.2 *Definitions of Terms Specific to This Standard:*

4.2.1 *measurement uncertainty, n—in the analysis of water*, a value representing the precision of a reported determination.

4.2.2 *water analysis measurement uncertainty, n—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.

4.3 *Symbols:*

4.3.1 *IQE*—Inter-Laboratory Quantitation Estimate

4.3.2 *LIMS*—Laboratory Information Management System

4.3.3 *MU*—Measurement Uncertainty

4.3.4 *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 Practice D6512, 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

[4] 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.

[5] Available from Bureau International des Poids et Mesures (BIMP), Pavillon de Breteuil F-92312 Sèvres Cedex, France, http://www.bipm.org.