

(or other reference matrix) to which a small amount of the analyte is added. This latter difference results from the fact that the concepts developed by Currie assume that measurements on blank samples will produce a signal that can be used to estimate measurement variability. This is the case with radiochemistry analyses, where there is usually some background radiation that produces a response in the analysis of a blank sample. For many other types of environmental analyses, the analysis of a blank sample produces no instrumental response. Thus, the EPA CWA MDL procedure involves adding the analyte to a reference matrix (e.g., a blank sample) at low concentrations to ensure that a response is produced.

2. Interlaboratory Detection Estimate (IDE) and Interlaboratory Quantitation Estimate (IQE)

The IDE was approved by ASTM International's Committee D 19 for Water in 1997, as ASTM Designation 6091-97: Standard Practice for 99%/95% Interlaboratory Detection Estimate (IDE) for Analytical Methods with Negligible Calibration Error. Subsequently, members of ASTM Committee D 19 developed the interlaboratory quantitation estimate (IQE) that was approved in 2000 as ASTM Designation D 6512-00: Standard Practice for Interlaboratory Quantitation Estimate. The IDE and IQE concepts are based on the variable error model and include procedures that require that data gathered in a formal study of a method be used to select from one of four possible models of the interlaboratory error and concentration. The possible models include: the "constant model," applicable to both the IDE and IQE, in which the interlaboratory standard deviation does not change with concentration; the "straight-line model," applicable to both the IDE and IQE, in which the interlaboratory standard deviation is a linear function of concentration; the "exponential model" applicable to the IDE, in which the interlaboratory standard deviation is an exponential function of concentration; and the "hybrid model" applicable to the IQE, in which the interlaboratory standard deviation has both additive (constant) and multiplicative (linear) components that follow the model of Rocke and Lorenzato (1995). Such studies involve samples representing at least five different concentration levels and analyzed in a minimum of six (required) to ten (recommended) laboratories. The ASTM procedures are also designed to take into account all possible sources of variability, including interlaboratory

variability, when estimating detection and quantitation limits. As a result, the IDE and IQE generally produce higher limits than are produced using other procedures.

D. Issues Considered During the Assessment

In performing the assessment, EPA identified a number of statistical and analytical chemistry issues that should be considered when evaluating detection and quantitation limit concepts and procedures in general, and in the specific context of Clean Water Act applications. The issues considered include six specific issues raised by the Petitioners and Intervenor, as well as issues identified by EPA staff, peer reviewers, and others. The six issues raised by the Petitioners are: Criteria for selection and appropriate use of statistical models; methodology for parameter estimation; statistical tolerance and prediction; criteria for design of detection and quantification studies, including selection of concentration levels ("spiking levels"); interlaboratory variability; and incorporation of elements of probability design.

Some of the significant additional issues considered by EPA in its assessment include: Matrix effects; minimization of false positives and false negatives; cost and ease of implementation; and how well detection and quantitation limits published in methods reflect individual laboratory capability. These and other issues considered by EPA are identified and discussed in Chapter 3 of the Assessment Document.

E. Evaluation Criteria

After identifying and considering the issues, EPA developed six evaluation criteria that reflect EPA's views concerning the issues. These six criteria formed the primary basis for evaluating the ability of each detection and quantitation limit approach identified in section III.C. above to meet EPA needs under the Clean Water Act. A complete discussion of these criteria and EPA's assessment of each approach against these criteria is provided in the Assessment Document that is available in the docket supporting this proposed rule. The six criteria are summarized below.

Criterion 1: The detection and quantitation limit approaches should be scientifically valid. In evaluating this criterion, EPA considered the following factors: (1) Whether the concept can be (and has been) tested; (2) whether the concept has been subjected to peer review and publication; (3) whether the

error rate associated with the concept or methodology is either known or can be estimated; (4) whether standards exist and can be maintained to control the concept's operation (i.e., it is supported by well-defined procedures for use); and (5) whether the concept has attracted (i.e., achieved) widespread acceptance within a relevant scientific community.

EPA believes that these considerations are helpful for demonstrating the scientific validity of a detection or quantitation concept.

Criterion 2: The approach should address demonstrated expectations of laboratory and method performance, including routine variability. EPA believes that the detection and quantitation limit procedures should be capable of providing a realistic expectation of laboratory performance. In evaluating different approaches against this criterion, EPA considered the sources of variability captured by the procedure and the degree to which the statistics that underlie the procedure realistically reflect these sources.

Criterion 3: The approach should be supported by a practical and affordable procedure that a single laboratory can use to evaluate method performance. Ideally, any required procedure for calculating analytical method sensitivity should be simple, complete, and cost-effective to implement. The laboratories that can be expected to use detection and quantitation procedures will range from large laboratories and laboratory chains with a wide range of technical capability to small laboratories operated by one or a few people with a limited set of statistical or analytical skills. If a procedure is complicated, it will be, generally, more error prone in its use. Similarly, if a procedure requires investment of extensive resources that cannot be billed to a client, laboratories will have a disincentive to use the procedure. Therefore, if EPA wishes to encourage the development and use of innovative techniques that improve measurement performance or lower measurement cost, the Agency should consider practicality and affordability as significant, if not co-equal, considerations to scientific validity.

Criterion 4: The detection level approach should identify the signal or estimated concentration at which there is 99% confidence that the substance is actually present when the analytical method is performed by experienced staff in a well-operated laboratory. Any approach to developing detection limits should be capable of providing regulators, the regulated community, and data users with confidence that a pollutant reported as being present really is present. Historically, nearly