

into a revised version of the Plan for the Assessment of Detection and Quantitation Limits Under Section 304(h) of the Clean Water Act (EPA 821-R-02-010, April, 2002; the "study plan"). The study plan is included in the docket for this proposal, along with the peer review comments and the Agency's response to them..

B. Information and Data used in the Assessment

In 1997 and 1998, EPA searched the published literature to identify documents that discussed detection and quantitation concepts and procedures. EPA conducted a follow-up search in 2001. The principal goal of these efforts was to identify concepts, procedures, and issues that should be considered by EPA during its assessment. EPA identified more than 100 documents describing detection and quantitation concepts and issues and has included a list of these documents in the docket supporting this proposed rule. Additional information concerning the literature search is presented and discussed in the Assessment Document.

EPA initially hoped to identify a large body of data containing a sufficient number of results that were generated at, below, and above the region of interest (*i.e.*, at concentration levels targeting limits of detection and quantitation). EPA determined, however, that few such data sets exist. EPA identified six useful data sets for fully evaluating measurement variability in the range of analytical detection and quantitation. These included three data sets generated by EPA expressly for the purpose of characterizing measurement variability in the region of interest and three data sets suggested by the Petitioners and Intervenor. Although the Petitioners and Intervenor suggested other data sets, EPA found that these data sets either did not include a sufficient number of data results that were at, below, and above the region of detection and quantitation to yield information for the assessment or that the data included in the data sets were of questionable validity. These data, and EPA's decisions regarding the data, are discussed in the Assessment Document.

As noted above, three of these studies were conducted by EPA for the purpose of evaluating the relationship between measurement variation and concentration. In these studies, replicate measurements from each combination of analyte and measurement technique (*i.e.*, analytical method) were produced by a single laboratory over a wide range and large number of concentrations. A fourth data set was developed as part of a study conducted by the American

Automobile Manufacturers Association (AAMA) for the purpose of estimating a quantitation value based on a concept called the alternative minimum level that had been described in the literature (Gibbons *et al.*, 1997). In that study, replicate samples were measured at a limited number of concentrations by multiple laboratories. The final two data sets were jointly gathered by EPA and the Electric Power Research Institute (EPRI) to support interlaboratory validation of EPA Methods 1631 and 1638.

Additional details concerning each of these studies are provided in the Assessment Document available in the docket supporting this proposed rule. Data from these studies also are available in the docket.

C. Concepts and Procedures Included in the Assessment

As mentioned earlier in this document, EPA identified numerous terms that have been used to describe the sensitivity of a particular method or instrument. Examples of these terms are analytical detection limit, lower limit of detection, limit of sensitivity, minimum detectable quantity, system detection limit, and approximate detection limit. For its assessment, EPA considered detection and quantitation terms, concepts, or procedures advanced in the published literature and by various EPA offices, the American Chemical Society (ACS), the International Union of Pure and Applied Chemistry (IUPAC), the International Organization for Standardization (ISO), ASTM International, industry groups, and others. EPA found that most of the terms or concepts considered have no corresponding definition or procedure for calculating a value, and it may be that these terms reflect the method developer's estimate of the lowest concentration of a substance that a test method is capable of measuring. EPA did not evaluate any such terms in the assessment. EPA also did not consider terms that do not reflect the entire measurement process (such as the "Instrument Detection Limit"), concepts that are uniquely designed for a single program (such as the "Contract Required Detection Limit" used in the Superfund Contract Laboratory Program), or concepts no longer advanced by the originating organization (such as the "Compliance Monitoring Detection Limit" and the "Alternative Minimum Level").

After eliminating terms and concepts for the reasons described above, EPA focused its assessment on four sets of concepts that are widely referenced and generally reflect the diversity of

concepts advanced to date. These include (1) The EPA MDL and ML used under CWA programs, (2) the Interlaboratory Detection Estimate (IDE) and Interlaboratory Quantitation Estimate (IQE) adopted by ASTM International, (3) the Limit of Detection (LOD) and Limit of Quantitation (LOQ) adopted by the American Chemical Society (ACS), and (4) the Critical Value (CRV), Minimum Detectable Value (MDV) and Limit of Quantification (LOQ) adopted by the International Union of Pure and Applied Chemistry (IUPAC) and the International Organization for Standardization (ISO). Although the ACS, IUPAC and ISO concepts are functionally similar to EPA's MDL and ML, these organizations have not developed detailed procedures for calculating detection and quantitation values. Only the EPA and ASTM concepts are supported by detailed procedures for calculating detection and quantitation values. Without such procedural details, the ACS, IUPAC and ISO concepts are unlikely to be useful for establishing detection and quantitation limits in analytical methods for use in CWA programs. Therefore, the discussion below addresses the EPA and ASTM concepts only. Results of EPA's evaluation of the additional concepts are discussed in detail in the Assessment Document included in the docket supporting this proposed rule.

1. Method Detection Limit (MDL) and Minimum Level (ML) of Quantitation

As discussed in section III.D of this document, the MDL is based on the constant error model proposed by Currie in 1968 and was initially promulgated in 1984 for use in CWA programs. The MDL and ML are supported by a procedure that involves the analysis of at least seven replicate samples containing the target analyte(s) at an estimate of the detection limit. Determination of the MDL is based on multiplication of the standard deviation among the replicate measurements by the 99th percentile of a t-distribution with $n-1$ degrees of freedom. The ML is also based on the constant error model proposed by Currie in 1968. The ML is derived by multiplying the standard deviation of the replicate measurements by 10. The primary differences between the MDL, ML, and detection and quantitation limit concepts first proposed by Currie are that (1) The MDL and ML are supported by detailed procedures for implementing the concepts, and (2) the EPA CWA procedures extend Currie's proposed replicate measurements of a blank with replicate measurements of reagent water