Alternative Methods of Compliance

(g)(1) An alternative method of compliance or adjustment of the compliance time that provides an acceptable level of safety may be used if approved by the Manager, Seattle ACO. Operators shall submit their requests through an appropriate FAA Principal Maintenance Inspector, who may add comments and then send it to the Manager, Seattle ACO.

(2) Alternative methods of compliance, approved previously per AD 94–15–12, amendment 39–8983, are approved as alternative methods of compliance with paragraphs (a) and (e) of this AD.

(3) Alternative methods of compliance, approved previously per AD 94–15–18, amendment 39–8989, are approved as alternative methods of compliance with paragraphs (b) and (e) of this AD.

(4) Alternative methods of compliance, approved previously per AD 94–15–18 and AD 94–15–12 that provide alternative inspections are approved as alternative methods of compliance for the inspections of that area only in this AD.

Note 6: Information concerning the existence of approved alternative methods of compliance with this AD, if any, may be obtained from the Seattle ACO.

Special Flight Permits

(h) Special flight permits may be issued per sections 21.197 and 21.199 of the Federal Aviation Regulations (14 CFR 21.197 and 21.199) to operate the airplane to a location where the requirements of this AD can be accomplished.

Issued in Renton, Washington, on March 5, 2003.

Ali Bahrami,

Acting Manager, Transport Airplane Directorate, Aircraft Certification Service.

[FR Doc. 03–5857 Filed 3–11–03; 8:45 am]

BILLING CODE 4910–13–P

DEPARTMENT OF LABOR

Mine Safety and Health Administration

30 CFR Part 75

RIN 1219–AA76

Underground Coal Mine Ventilation—Safety Standards for the Use of a Belt Entry as an Intake Air Course To Ventilate Working Sections and Areas Where Mechanized Mining Equipment Is Being Installed or Removed

AGENCY: Mine Safety and Health Administration (MSHA), Labor.

ACTION: Change of hearing dates.

SUMMARY: MSHA published hearing dates in the January 27, 2003 proposed rule on Safety Standards for the Use of a Belt Entry as an Intake Air Course to Ventilate Working Sections and Areas Where Mechanized Mining Equipment Is Being Installed or Removed (68 FR 3936). Three of the hearing dates published with the proposed rule conflict with other Agency hearings and are being changed. The hearing in Grand Junction, Colorado is changed from May 29, 2003 to April 3, 2003. The hearing in Charleston, West Virginia is changed from May 13, 2003 to April 8, 2003. The hearing in Washington, Pennsylvania is changed from May 15, 2003 to April 10, 2003. All of the hearing locations are printed under **SUPPLEMENTARY INFORMATION** for the convenience of the public.

FOR FURTHER INFORMATION CONTACT: Marvin W. Nichols, Jr., Director; Office of Standards, Regulations, and Variances, MSHA; phone: (202) 693–9440; facsimile: (202) 693–9441; E-mail: *nichols-marvin@msha.gov.*

SUPPLEMENTARY INFORMATION:

I. Public Hearings

The table contains information on the hearing dates, locations, and phone numbers for all of the hearings on ''Safety Standards for the Use of a Belt Entry as an Intake Air Course to Ventilate Working Sections and Areas Where Mechanized Mining Equipment is Being Installed or Removed.''

Date	Location	Phone
April 3, 2003	Holiday Inn Grand Junction, 755 Horizon Drive, Grand Junction, CO 81506	(970) 243–6790
April 8, 2003	Marriott Town Center, 200 Lee Street, Charleston, WV 25301	(304) 345–6500
April 10, 2003	Holiday Inn at the Meadows, 340 Racetrack Road, Washington, PA 15301	(724) 222–6200
April 29, 2003	Holiday Inn—Birmingham Airport, 5000 10th Avenue North, Birmingham, AL 35212	(205) 591–6900
May 1, 2003	Holiday Inn Lexington—North, 1950 Newton Pike, Lexington, KY 40305	(859) 233–0512

Dated: March 7, 2003.

Dave D. Lauriski,

Assistant Secretary of Labor for Mine Safety and Health.

[FR Doc. 03–5942 Filed 3–11–03; 8:45 am]

BILLING CODE 4510–43–P

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 136

[FRL–7463–1]

RIN 2040–AD53

Guidelines Establishing Test Procedures for the Analysis of Pollutants; Procedures for Detection and Quantitation

AGENCY: Environmental Protection Agency (EPA).

ACTION: Proposed rule.

SUMMARY: This action proposes revisions to the procedures for determining the sensitivity of analytical (test) methods under EPA's Clean Water Act (CWA). EPA's method detection limit (MDL) and minimum level of quantitation (ML) are used to define test sensitivity under the CWA. The MDL is used to determine the lowest concentration at which a substance is detected or is ''present'' in a sample. The ML appears in many EPA methods and has been used to describe the lowest concentration of a substance that gives a recognizable signal, or as a quantitation limit. The proposed revisions include clarifications and improvements that are based on a recent EPA assessment of the MDL and the ML and of alternative approaches for defining test sensitivity, peer review of the Agency's assessment, and earlier stakeholder comments on the existing MDL procedure. This proposal also revises the definition of the MDL to reflect the proposed revisions to the procedure. The Agency's assessment of existing EPA procedures for determining test sensitivity and alternative approaches is also made available for public comment in a separate notice in today's **Federal Register** (see Notice of Document Availability and Public Comment Period on the Technical Support Document for the Assessment of Detection and Quantitation Concepts).

DATES: Comments must be postmarked, delivered by hand, or electronically mailed on or before July 10, 2003. Comments provided electronically will be considered timely if they are submitted electronically by 11:59 p.m. Eastern Time on July 10, 2003.

ADDRESSES: Comments may be submitted by mail to Water Docket, U.S. Environmental Protection Agency (4101T), 1200 Pennsylvania Avenue NW., Washington DC 20460, or electronically through EPA Dockets at

http://www.epa.gov/edocket/, Attention Docket ID No. OW–2003–0002. See Unit C of the **SUPPLEMENTARY INFORMATION** section for additional ways to submit comments and more detailed instructions.

FOR FURTHER INFORMATION CONTACT: William Telliard; Engineering and Analysis Division (4303T); Office of Science and Technology; Office of Water; U.S. Environmental Protection Agency; Ariel Rios Building; 1200 Pennsylvania Avenue, NW.; Washington, DC 20460, or call (202) 566–1061 or E-mail at *telliard.william@epa.gov*.

SUPPLEMENTARY INFORMATION:

A. Potentially Regulated Entities

EPA Regions, as well as States, Territories and Tribes authorized to implement the National Pollutant Discharge Elimination System (NPDES) program, issue permits that comply with the technology-based and water quality-based requirements of the Clean Water Act (CWA). In doing so, NPDES permitting authorities, including States, Territories, and Tribes, make several discretionary choices when they write the permit. These choices include the selection of pollutants to be measured and, in many cases, limited in permits. If EPA has ''approved'' (*i.e.*, promulgated through rulemaking) standardized testing procedures under 40 CFR part 136 for the analysis of a given pollutant, the NPDES permit must include one of the approved testing procedures or an approved alternate test procedure. The testing procedures can include a specification for detection and quantitation levels that must be met. Therefore, entities with NPDES permits could potentially be regulated by the proposed revisions to the detection and quantitation procedures in this rulemaking. In addition, when an authorized State, Territory, or Tribe certifies Federal licenses under CWA section 401, they must use the standardized testing procedures and meet the associated detection and quantitation levels. Categories and entities that could potentially be regulated include:

Category	Examples of potentially regulated entities
State, Territorial, and Indian Tribal Governments	States, Territories, and Tribes authorized to administer the NPDES permitting program; States, Territories, and Tribes providing certification under Clean Water Act section 401
Industry	Facilities that must conduct monitoring to comply with NPDES permits
Municipalities	POTWs that must conduct monitoring to comply with NPDES permits

This table is not intended to be exhaustive, but rather provides a guide for readers regarding entities likely to be regulated by this action. This table lists the types of entities that EPA is now aware could potentially be regulated by this action. Other types of entities not listed in the table could also be regulated. If you have questions regarding the applicability of this action to a particular entity, consult the person listed in the preceding **FOR FURTHER INFORMATION CONTACT** section.

B. How Can I Get Copies of This Document and Other Related Information?

1. *Docket*. EPA has established an official public docket for this action under Docket ID No. OW–2003–0002. The official public docket consists of the documents specifically referenced in this action, any public comments received, and other information related to this action. Although a part of the official docket, the public docket does not include Confidential Business Information (CBI) or other information whose disclosure is restricted by statute. The official public docket is the collection of materials that is available for public viewing at the Water Docket in the EPA Docket Center, EPA West Building, Room B102, 1301 Constitution Avenue NW., Washington, DC. The EPA Docket Center Public Reading Room is open from 8:30 a.m. to 4:30 p.m., Monday through Friday, excluding legal holidays. The telephone number for the Public Reading Room is (202) 566–1744, and the telephone number for the Water Docket is (202) 566–2426.

2. *Electronic Access*. You may access this **Federal Register** document electronically through the EPA Internet under the ''**Federal Register**'' listings at*http://www.epa.gov/fedrgstr/*. An electronic version of the public docket is available through EPA's electronic public docket and comment system, EPA Dockets. You may use EPA Dockets at *http://www.epa.gov/edocket/* to submit or view public comments, to access the index listing of the contents of the official public docket, and to access those documents in the public docket that are available electronically. Once in the system, select ''search,'' then key in the appropriate docket identification number.

Certain types of information will not be placed in the EPA Dockets. Information claimed as CBI and other information whose disclosure is restricted by statute, which is not included in the official public docket, will not be available for public viewing in EPA's electronic public docket. EPA's policy is that copyrighted material will not be placed in EPA's electronic public docket but will be available only in printed, paper form in the official public docket. Although not all docket materials may be available electronically, you may still access any of the publicly available docket materials through the docket facility identified in B.1.

For public commenters, it is important to note that EPA's policy is that public comments, whether submitted electronically or in paper, will be made available for public viewing in EPA's electronic public docket as EPA receives them and without change, unless the comment contains copyrighted material, CBI, or other information whose disclosure is restricted by statute. When EPA identifies a comment containing copyrighted material, EPA will provide a reference to that material in the version of the comment that is placed in EPA's electronic public docket. The entire printed comment, including the copyrighted material, will be available in the public docket.

Public comments submitted on computer disks that are mailed or delivered to the docket will be transferred to EPA's electronic public docket. Public comments that are mailed or delivered to the Docket will be scanned and placed in EPA's electronic public docket. Where practical, physical objects will be photographed, and the photograph will be placed in EPA's electronic public docket along with a brief description written by the docket staff.

C. How and to Whom Do I Submit Comments?

You may submit comments electronically, by mail, or through hand delivery/courier. To ensure proper receipt by EPA, identify the appropriate docket identification number in the subject line on the first page of your comment. Please ensure that your

comments are submitted within the specified comment period. Comments received after the close of the comment period will be marked ''late.'' EPA is not required to consider these late comments. However, late comments may be considered if time permits.

1. *Electronically*. If you submit an electronic comment as prescribed below, EPA recommends that you include your name, mailing address, and an e-mail address or other contact information in the body of your comment. Also include this contact information on the outside of any disk or CD ROM you submit, and in any cover letter accompanying the disk or CD ROM. This ensures that you can be identified as the submitter of the comment and allows EPA to contact you in case EPA cannot read your comment due to technical difficulties or needs further information on the substance of your comment. EPA's policy is that EPA will not edit your comment, and any identifying or contact information provided in the body of a comment will be included as part of the comment that is placed in the official public docket, and made available in EPA's electronic public docket. If EPA cannot read your comment due to technical difficulties and cannot contact you for clarification, EPA may not be able to consider your comment.

i. EPA Dockets. Your use of EPA's electronic public docket to submit comments to EPA electronically is EPA's preferred method for receiving comments. Go directly to EPA Dockets at *http://www.epa.gov/edocket*, and follow the online instructions for submitting comments. Once in the system, select ''search,'' and then key in Docket ID No. OW–2003–0002. The system is an ''anonymous access'' system, which means EPA will not know your identity, e-mail address, or other contact information unless you provide it in the body of your comment.

ii. E-mail. Comments may be sent by electronic mail (e-mail) to: *OW-docket@epamail.epa.gov*, Attention Docket ID No. OW–2003–0002. In contrast to EPA's electronic public docket, EPA's e-mail system is not an ''anonymous access'' system. If you send an e-mail comment directly to the Docket without going through EPA's electronic public docket, EPA's e-mail system automatically captures your e-mail address. E-mail addresses that are automatically captured by EPA's e-mail system are included as part of the comment that is placed in the official public docket, and made available in EPA's electronic public docket.

iii. Disk or CD ROM. You may submit comments on a disk or CD ROM that you mail to the mailing address identified in Unit C.2. These electronic submissions will be accepted in WordPerfect or ASCII file format. Avoid the use of special characters and any form of encryption.

2. *By Mail*. Send an original and three copies of your comments to Water Docket, U.S. Environmental Protection Agency (4101T), 1200 Pennsylvania Avenue NW., Washington, DC 20460, Attention Docket ID No. OW–2003–0002.

3. *By Hand Delivery or Courier*. Deliver your comments to the Water Docket Center, EPA West Building, Room B102, 1301 Constitution Avenue NW., Washington, DC, Attention Docket ID No. OW–2003–0002. Such deliveries are only accepted during the Docket's normal hours of operation as identified in Unit B.1.

C. How Should I Submit CBI to the Agency?

Do not submit information that you consider to be CBI electronically through EPA's electronic public docket or by e-mail. You may claim information that you submit to EPA as CBI by marking any part or all of that information as CBI (if you submit CBI on disk or CD ROM, mark the outside of the disk or CD ROM as CBI and then identify electronically within the disk or CD ROM the specific information that is CBI). Information so marked will not be disclosed except in accordance with procedures set forth in 40 CFR part 2.

In addition to one complete version of the comment that includes any information claimed as CBI, a copy of the comment that does not contain the information claimed as CBI must be submitted for inclusion in the public docket and EPA's electronic public docket. If you submit the copy that does not contain CBI on disk or CD ROM, mark the outside of the disk or CD ROM clearly that it does not contain CBI. Information not marked as CBI will be included in the public docket and EPA's electronic public docket without prior notice. If you have any questions about CBI or the procedures for claiming CBI, please consult the person identified in the **FOR FURTHER INFORMATION CONTACT** section.

D. What Should I Consider as I Prepare My Comments for EPA ?

You may find the following suggestions helpful for preparing your comments:

1. Explain your views as clearly as possible.

2. Describe any assumptions that you used.

3. Provide any technical information and/or data you used that support your views.

4. If you estimate potential burden or costs, explain how you arrived at your estimate.

5. Provide specific examples to illustrate your concerns.

6. Offer alternatives.

7. Make sure to submit your comments by the comment period deadline.

8. Ensure proper receipt by EPA by identifying the appropriate docket identification number in the subject line on the first page of your response. It would also be helpful if you provided the name, date, and **Federal Register** citation related to your comments.

Outline of Document

I. Statutory Authority

This action is being proposed pursuant to the authority of sections 301(a), 304(h), and 501(a) of the Clean Water Act (''CWA'' or the ''Act''), 33 U.S.C. 1311(a), 1314(h), 1361(a). Section 301(a) of the Act prohibits the discharge of any pollutant into navigable waters unless the discharge complies with a National Pollutant Discharge Elimination System (NPDES) permit issued under section 402 of the Act. Section 304(h) of the Act requires the Administrator of the EPA to ''promulgate guidelines establishing test procedures for the analysis of pollutants that shall include the factors which must be provided in any certification pursuant to [section 401 of this Act] or permit application pursuant to [section 402 of this Act].'' Section 501(a) of the Act authorizes the Administrator to ''prescribe such regulations as are necessary to carry out this function under [the Act].'' EPA publishes analytical test method regulations for use in CWA programs at 40 CFR part 136. The Administrator has made these test methods applicable to monitoring and reporting of NPDES permits (40 CFR 122.21, 122.41, 122.44, and 123.25), and implementation of the pretreatment standards issued under section 307 of the Act (40 CFR 403.10 and 403.12).

II. Purpose of This Action

EPA recently completed an assessment of procedures for determining the sensitivity of analytical test methods (*i.e.*, procedures for determining detection and quantitation) and their application to Clean Water Act Programs. That assessment was conducted pursuant to a settlement agreement with the Alliance of Automobile Manufacturers, *et al.* (See III.B. below for details.) The assessment is contained in a document entitled, Technical Support Document for the Assessment of Detection and Quantitation Concepts or ''Assessment Document'' (EPA 821–R–03–005, February, 2003). A draft of the Assessment Document was peer-reviewed in August 2002 in accordance with EPA peer review guidelines. Following peer review, EPA incorporated peer review comments into the Assessment Document. EPA is providing an opportunity for public review and comment on the assessment and the Assessment Document through this notice and also in a separate notice in this **Federal Register** (see Notice of Document Availability and Public Comment Period on the Technical Support Document for the Assessment of Detection and Quantitation Concepts).

Based on findings from the assessment, EPA is proposing revisions to the method detection limit procedure codified at 40 CFR part 136, Appendix B and is seeking comment on the revisions proposed in this notice. EPA also is proposing to revise the definition of ''Detection limit'' at 40 CFR 136.2 and to add a definition of the ''Minimum level of quantitation (ML)'' for consistency with the proposed revisions to Appendix B.

III. Background

A. Analytical (Test) Methods Used for CWA Programs

Section 304(h) of the Clean Water Act requires that the EPA Administrator ''promulgate guidelines establishing test procedures for the analysis of pollutants'' to be monitored and regulated under the National Pollutant Discharge Elimination System (NPDES). EPA proposes and promulgates test methods at 40 CFR part 136 in accordance with section 304(h). The approved test methods have been drawn from a variety of sources, including methods developed by commercial vendors, EPA and other government agencies, as well as methods from voluntary consensus standards bodies (VCSBs), such as the American Public Health Association (APHA), the Water Environment Federation (WEF), and the American Water Works Association (AWWA), which jointly publish Standard Methods for the Examination of Water and Wastewater; the Association of Official Analytical Chemists (AOAC-International); and the American Society for Testing and Materials (ASTM International).

Among considerations for approval of a test method at 40 CFR part 136 are the demonstrated performance characteristics of precision, bias, and sensitivity (*i.e.*, detection and quantitation). EPA generally evaluates each of these characteristics to determine if the test method will yield results at concentrations of concern that are reliable enough to meet EPA needs for permitting and compliance monitoring under the CWA. Detection and quantitation limits have been among the most controversial of these characteristics, particularly among members of the regulated community.

B. Settlement Agreement

On June 8, 1999, EPA published a final rule adding EPA Method 1631, Revision B: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry (Method 1631B) to the ''Guidelines Establishing Test Procedures for the Analysis of Pollutants'' under section 304(h) of the Clean Water Act. This method was developed specifically to measure concentrations of mercury at low (*i.e.*, ambient water quality criteria) levels. Following promulgation, the Alliance of Automobile Manufacturers, the Chemical Manufacturers Association, and the Utility Water Act Group (''Petitioners'') and the American Forest and Paper Association (''Intervenor'') filed a lawsuit challenging the method. *(Alliance of Automobile Manufacturers, et al.* v. *EPA,* No. 99–1420 (D.C. Cir.)). The challenge addressed specific aspects of EPA Method 1631 as well as the general procedures used to establish the method detection limit (MDL) and the minimum level of quantitation (ML) specified in the method. On October 19, 2000, EPA entered into a settlement agreement with the Petitioners and Intervenor (the ''settlement agreement''). The settlement agreement included six clauses. EPA has already satisfied the requirements of clauses 1 through 5, which addressed clarification and revision of specific method procedures and requirements. This proposal partially fulfills the requirements of clause 6 of the settlement agreement, which addresses procedures for determining the sensitivity of analytical test methods.

Clause 6 provides for EPA to assess existing Agency and alternative procedures for determining detection and quantitation limits under the Clean Water Act and to sign a notice for publication in the **Federal Register** on or before February 28, 2003, inviting public comment on the assessment. The assessment is to include, at a minimum, evaluation of the ''Definition and Procedure for Determination of the Method Detection Limit'' published at 40 CFR part 136, Appendix B and used in Method 1631, and evaluation of the corresponding ''minimum level'' of quantitation procedures.

Clause 6 further provides for EPA to submit its assessment to formal peer review by experts in the field of analytical chemistry and in the statistical aspects of analytical data interpretation. EPA conducted peer review of its assessment in August 2002. A summary of the results of the peer review is provided in section VI of this proposal; the peer reviewers' comments and EPA's responses are included in the docket for this proposal. As stipulated in the settlement agreement, EPA

provided the draft Assessment Document to the Petitioners and Intervenor for concurrent review and comment in August 2002. Their comments are also included in the docket for this proposal.

Finally, EPA agreed to invite public comment on the assessment for a period of no less than 120 days and to sign a notice taking final action on the assessment on or before September 30, 2004. Elsewhere in today's **Federal Register**, EPA is publishing a notice of availability of the Assessment Document, titled ''Technical Support Document for the Assessment of Detection and Quantitation Concepts,'' and announcing a 120-day comment period on it.

C. Detection, Quantitation, and Current Controversy

Generally speaking, a detection limit is the lowest concentration or amount of a substance that allows for differentiation between a sample that contains the substance and one that does not. A quantitation limit is the lowest concentration or amount of a substance that can be measured with some stated level of confidence. Establishing such detection and quantitation limits generally involves the application of statistics and chemistry expertise and judgement. The fact that scientific judgement is involved in the detection and quantitation decision is evidenced by the continuing debate on this subject; the number of different terms currently in use by different organizations; the number of concepts and procedures that have been advanced by different organizations to define or determine the detection and quantitation capabilities of analytical test methods; and the fact that there is no general consensus among various government agencies, method developers, or scientific organizations on a single detection and quantitation approach. EPA estimates that more than 50 different terms have been used in published analytical test methods to describe detection and quantitation capabilities of test methods and, in many instances, the same term is used by different organizations to mean different things.

Nearly all of the approaches advanced to date fall into one of two main categories: (1) Those that assume measurement error is constant or effectively constant in the low concentration range and are, therefore, based on the error observed in replicate measurements made at a single low concentration, and (2) those that assume measurement error varies as a function of concentration and are, therefore, based on the error observed in replicate measurements gathered in the region of detection and quantitation. Examples of the first category (referred to as the ''single concentration approach'' or ''constant error model'') include those first advanced by Lloyd Currie (1968) and later adopted in various forms by the American Chemical Society (ACS), the International Organization for Standardization (also known as ''ISO''), the International Union of Pure and Applied Chemistry (IUPAC), and EPA. Examples of the latter category (the ''variable error model'') were adopted in various forms by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA, now the U.S. Army Environmental Center, or USAEC) and ASTM International. The two categories represent two somewhat different conceptual approaches to the problem of assessing detection and quantitation capabilities. Both approaches require estimates of measurement variability in the low concentration range, but the philosophy behind the first category is based on direct measurement of variability at a fixed concentration in the concentration region most relevant to the problem. The philosophy behind the second category is based on the concept that measurement variability throughout the low end of the measurement range is relevant to the problem of setting detection and quantitation limits. The methodology used in implementing procedures in the second category involves statistical estimation methods that allow data collected throughout the low end of the range to contribute to estimation of measurement variability in detection and quantitation region.

There are also differences in the experimental procedures used to determine detection and quantitation limits. Again, these tend to fall into two categories. The first category of single-laboratory detection limits uses data from an experiment in a single laboratory to estimate detection limits. The second category of multi-laboratory detection limits uses data from experiments from multiple laboratories to estimate detection limits. The rationale for the latter proposal is that actual measurement sensitivity varies among laboratories, regardless of the approach used to estimate the sensitivity of a given method. The Interlaboratory Detection Estimate (IDE) and the Interlaboratory Quantitation Estimate (IQE) adopted by ASTM International is an example of such an approach. Although EPA's MDL procedure does not incorporate specific procedures to account for multiple laboratory variability, EPA nonetheless has accounted for this variability during method validation as described in Section D.1 below.

D. Historical Use of Detection and Quantitation Limits Under the Clean Water Act

The procedure for estimating the MDL was originally published in 1981 by staff at EPA's environmental research laboratory in Cincinnati, Ohio (Glaser, *et al.*, 1981). The MDL is based on the constant error model described by Currie (1968). EPA promulgated the procedure for determining the MDL for use in CWA programs on October 26, 1984 (49 FR 43234).

The ML was originally proposed on December 5, 1979 (44 FR 69463), in footnotes to Table 2 of EPA Method 624 and to Tables 4 and 5 of EPA Method 625. Between 1980 and 1984, EPA developed Methods 1624 and 1625 and included the ML in similar tables in those two methods. When these four methods were promulgated for use in CWA programs on October 26, 1984 (49 FR 43234), EPA replaced the MLs in Methods 624 and 625 with MDLs, and retained the MLs in Methods 1624 and 1625. Unlike the MDL, there have been changes to the definition of the ML over the years. For example, the term ''recognizable signal'' has been used instead of ''recognizable mass spectra'' for non-GC/MS methods.

Since 1984, the MDL and ML have been used in a variety of ways by analytical laboratories, permitting authorities, and regulatory communities. The three most significant uses of the MDL are described below, along with some concerns with those uses.

1. Method Development

The primary purpose of the MDL and ML is to characterize the sensitivity of a particular test method for a particular pollutant. Information about method sensitivity is critical when deciding which method is needed to accomplish a specific measurement objective.

The MDLs published in some EPA methods have been criticized because they are based on the performance of a single laboratory that may not reflect the capabilities of the laboratory community. EPA has responded to this criticism in recent years by gathering MDL information from multiple laboratories. During development of several analytical methods, EPA's Office of Science and Technology addressed the issue by using single laboratory studies to develop an initial estimate of the MDL for each analyte and then verified these MDLs in interlaboratory

studies or in additional single-laboratory studies at other facilities. For example, when EPA initially drafted Method 1631 for measurement of mercury, EPA estimated the MDL to be 0.05 ng/L, based on results produced by a contract research laboratory. Additional single-laboratory studies suggested that the MDL should be raised to 0.2 ng/L to better reflect existing capabilities of the laboratory community. During EPA's interlaboratory study for Method 1631, twelve participant laboratories were asked to conduct MDL studies. Each laboratory obtained an MDL less than 0.2 ng/L, the value published in the promulgated version of Method 1631.

The ML has been used in the 1600-series of EPA chemical methods promulgated for use under the CWA since 1984 as an additional means to characterize method sensitivity, establish the lower end of the calibration range, and serve as a quantitation limit in those methods. Although its use has thus far been limited to the 1600-series methods, the ML concept is applicable to any analytical procedure to which the MDL can be applied under the CWA.

2. Demonstrating Laboratory Performance

The MDL also has been used as a means of demonstrating laboratory capability or performance. For example, a laboratory often publishes results of an MDL study to advertise its ability to detect a pollutant at a low level. Similarly, a laboratory client or a certification program may require that a laboratory demonstrate its ability to achieve a specified MDL using a particular method.

EPA also has used MDLs in approved EPA CWA methods (*i.e.*, promulgated at 40 CFR part 136) to provide a standard for allowing increased flexibility and encouraging advances in technology. Under EPA's CWA Alternate Test Procedures (ATP) program and in EPA's performance-based methods, a laboratory is permitted to modify certain aspects of approved method procedures provided that it is able to achieve an MDL that is less than or equal to one-third the regulatory compliance limit or less than or equal to the MDL specified in the approved method, whichever is greater (see section 9.0 of EPA Method 1631, for example).

3. Use of the MDL and ML in Clean Water Act Programs

Both the MDL and ML have been used as reporting limits for a variety of studies and monitoring efforts under the CWA. For example, EPA often uses the MDL as a reporting threshold in surveys designed to determine levels of human exposure from consumption of water or fish under the CWA in order to characterize health risks from a variety of pollutants. In recent years, EPA has used the ML as the reporting limit in setting numeric limits for effluent guidelines limitations. EPA recommended in a 1994 draft guidance document that the ML be included in a National Pollutant Discharge Elimination System (NPDES) permit as a footnote to the water quality-based effluent limit (WQBEL) when the WQBEL is below either the MDL or ML of the most sensitive method. (See U.S. EPA Draft National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-based Effluent Limitations Set Below Analytical Detection/Quantitation Levels, 1994.) This 1994 draft guidance document was very controversial and was never finalized. Because individual States are responsible for implementation and enforcement of NPDES permits, use of the MDL and ML in the NPDES program varies among the States.

4. Concerns Regarding Use of the MDL

Over the years, a number of concerns have been raised about the MDL procedure. Some of these concerns are technical in nature (*e.g.*, selection of appropriate spiking levels and treatment of outliers), while others focus on implementation (*e.g.*, use of the MDL as a regulatory compliance limit). As part of EPA's assessment of detection and quantitation limits, the Agency identified and investigated a number of issues, including concerns that had been presented to the Agency by a variety of sources (*e.g.*, commercial laboratories, permittees, State laboratory and permitting authorities, EPA and other Federal laboratories, and others). Section IV.D of this proposal highlights the most significant issues addressed during the recent assessment. A comprehensive discussion of these issues is provided in the Assessment Document that is available in the docket supporting today's proposed rule and noticed elsewhere in today's **Federal Register** for public comment.

IV. EPA's Assessment of Detection and Quantitation Concepts

EPA first began a comprehensive assessment of detection and quantitation limits in the mid-1990s as concerns about the increased use of water quality-based permitting began to push permit limits for many pollutants below the measurement capabilities of some laboratories for a number of environmental chemistry methods. One of the key areas of concern centered on the nature of measurement error in the region of detection and quantitation. Because EPA was not aware of studies that included replicate testing across or within the vicinity of this region, EPA focused its early efforts on developing such data, first with a single-laboratory study of measurement error using inductively coupled plasma-mass spectrometry (ICP-MS) techniques, and later with a similar single-laboratory study of measurement error using 10 different analytical techniques commonly used in Clean Water Act monitoring programs.

The October 2000 settlement agreement described in section III.B. of this preamble committed EPA to a fixed timetable and established specific milestones for completing its assessment. The general approach used in the Agency's assessment of detection and quantitation concepts and procedures is summarized below. Additional details concerning the assessment are presented in the Assessment Document that is available in the public docket supporting this proposed rule. EPA is also providing an opportunity for public review and comment on this assessment and the Assessment Document in a separate notice in today's **Federal Register** (see Notice of Document Availability and Public Comment Period on the Technical Support Document for the Assessment of Detection and Quantitation Concepts).

A. Study Plan

In December of 2001, EPA produced a draft Plan for the Assessment of Detection and Quantitation Limits Under Section 304(h) of the Clean Water Act. The December 2001 plan described roles and responsibilities for implementing the plan, provided a background discussion of detection and quantitation limit concepts, and outlined a series of events necessary to support EPA's assessment of detection and quantitation concepts and procedures as required to comply with the terms and schedules set forth in Clause 6 of the settlement agreement.

The draft plan was circulated for review by EPA staff, the Petitioners and Intervenor, and external peer reviewers. The external peer review was performed in accordance with EPA's Science Policy Council Handbook—Peer Review, 2nd Edition (EPA 100–B–00–001, December 2001; the ''Peer-review Handbook''). EPA evaluated the comments and recommendations provided by reviewers and, where appropriate, integrated these comments

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

(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% Interlabortory 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

every detection limit approach has set the criterion for detection at 99 percent confidence (i.e., the lowest level at which a pollutant will be detected with a probability of 99 percent). This criterion results in the probability of a false positive; i.e., that a pollutant will be stated as being present when it is not really present (a Type I error), of one percent.

Criterion 5: The quantitation limit approach should identify the concentration that gives a recognizable signal that is consistent with the capabilities of the method when a method is performed by experienced staff in well-operated laboratories. Measurement capabilities among laboratories vary depending on a number of factors, including, but not limited to, instrumentation, training, and experience. Similarly, measurement capabilities among different analytical methods vary depending on a number of factors, including the techniques and instrumentation employed and the clarity of the method itself. Historical approaches to recognizing laboratory capabilities in establishing detection and quantitation limits have varied between two extremes of establishing the limit in a state-of-the-art research laboratory to reflect the lowest possible limit that can be achieved, and establishing the limit based on statistical prediction intervals calculated from a large number of laboratories with varying levels of experience, instrumentation and competence. Generally, use of the former has been employed to serve as a goal or performance standard to be met by other laboratories, whereas use of the latter treats the limit, not as a performance standard that needs to be met by each laboratory, but rather as a characterization of the future performance of the entire universe of laboratory capabilities at the time of method development. Rather than using one of these two extremes, EPA prefers to establish a quantitation limit at a concentration that is achievable with a defined level of confidence in well-operated laboratories.

Criterion 6: Detection and quantitation approach should be applicable to the variety of decisions made under the Clean Water Act, and should support State and local obligations to implement measurement requirements that are at least as stringent as those set by the Federal Government. The Clean Water Act requires EPA to conduct, implement, and oversee a variety of data gathering programs. These programs include, but are not limited to, surveys to monitor changes in ambient water quality, screening studies to identify pollutants of concern, data gathering to support effluent guidelines, environmental assessments to establish water quality standards, and studies to evaluate human health and environmental risks under the Clean Water Act. In addition, EPA should be able to apply detection and quantitation limits to permitting, quality control in analytical laboratories, method promulgation, and other uses of the 40 CFR part 136 methods.

V. EPA's Findings and Conclusions

As noted previously, EPA considered four sets of detection and quantitation limit approaches advanced by EPA, ASTM International, ACS, and both ISO and IUPAC. Each approach was assessed against the suite of criteria described above for use under the Clean Water Act. The EPA approaches (*i.e.,* the MDL and ML) and the ASTM International approaches (*i.e.,* the IDE and IQE) are supported by clearly defined procedures for implementing the concepts. Neither the ACS nor the ISO/IUPAC approaches are supported by detailed procedures for implementation; this lack of supporting procedures was reflected in the outcome of EPA's overall assessment. Briefly, EPA found that (1) no single pair of detection and quantitation limit concepts perfectly meets EPA's criteria for use under the Clean Water Act, (2) the MDL and ML most closely meet EPA's criteria, and (3) minor revisions and clarifications to the MDL and ML would allow both concepts to fully meet the Agency's needs under the CWA. Details of these revisions and clarifications are described in section VII of this proposed rule. EPA also found that, although the IDE and IQE procedures may be acceptable for establishing detection and quantitation values derived from interlaboratory validation studies, the complexity and subjectivity of the procedures, along with their inability to address individual laboratory performance, make them unsuitable as the primary means of establishing sensitivity under the Clean Water Act. However, EPA believes that the IDE and IQE can be used to establish sensitivity under certain conditions. EPA would be willing to consider and approve under 40 CFR part 136, new test methods that include the IDE and IQE. Details of EPA's findings are provided in the Assessment Document that is available in the docket supporting this proposed rule.

VI. Peer Review of EPA's Assessment

In August 2002, EPA conducted a peer review of its assessment as presented in a draft Technical Support Document (draft Assessment Document). The peer review was performed in accordance with EPA's peer review policies, which are described in the Science Policy Council Handbook (EPA 100–B–00–001), and performed by two experts in the field of analytical chemistry and two experts in the statistical aspects of analytical data interpretation. Reviewers were provided with a draft copy of EPA's Assessment Document, copies of all data evaluated in the assessment, statistical programs used to analyze the data, and copies of the detection and quantitation approaches evaluated.

In the charge to the peer reviewers, EPA requested a written evaluation of whether the assessment approach described by EPA is valid and of the conceptual soundness of the assessment. Reviewers also were asked to consider and address eight specific questions pertaining to the adequacy of the concepts and procedures, the issues considered, the evaluation criteria developed by EPA, EPA's assessment and conclusions, the data used to perform the assessment, suggested improvements to the procedures discussed, and EPA's consideration of interlaboratory vs. intralaboratory issues. A copy of all materials associated with the peer review, including the peer review charge, the materials provided to the peer reviewers for review, complete copies of the peer reviewers' comments, and detailed EPA responses to each of the comments is provided in the docket supporting this proposed rule.

The comments from the peer reviewers were generally supportive of EPA's assessment and its presentation of the assessment in the draft Assessment Document. The peer reviewers stated that EPA's assessment of detection and quantitation concepts appears valid based on the evaluation criteria and is consistent with the Data Quality Act and EPA's Quality System. The peer reviewers stated further that the detection and quantitation concepts and procedures considered, the issues addressed, and the evaluation criteria developed based on those issues are sufficiently complete and adequate. Although two of the four peer reviewers believe that the use of interlaboratory measurements is important for a general understanding of the laboratory communities' capabilities, they also believe that the MDL and ML are more appropriate to address the issues that

EPA must consider in support of a permittee's CWA requirements. These commenters concluded that EPA's approach between inter- and intra-laboratory studies is balanced and reasonable. Overall, the peer reviewers supported the continued use of the MDL and ML procedures, almost to the exclusion of the other approaches. The most notable exception was a suggestion that EPA consider abandoning the ''traditional'' concept of a quantitation limit, such as the ML, and instead consider that any measured result reported with an associated estimate of measurement precision is a quantifiable value. Reviewers stated, however, that use of the ML is practical if EPA desires to establish a quantitation limit.

Although the peer reviewers were generally supportive of the assessment and EPA's current approach to detection and quantitation under the CWA, they had some recommendations for improvement to the Agency's assessment and to the MDL procedure. The reviewers suggested that EPA consider the following: (1) Providing additional references; (2) expanding the discussion of outliers; (3) establishing a repository of reference materials that demonstrate the ability to handle interferences and low level detection; (4) making minor modifications to Evaluation Criterion 4 (i.e., edit to reflect equivalence to an implementation of Currie's critical level); (5) clarifying the MDL confidence interval calculations discussed in Chapter 5 of the Assessment Document; and (6) enhancing the focus on the impact of operational procedures (quality control) in method performance. The Assessment Document available in the docket supporting today proposed rule addresses each of these suggestions.

The peer reviewers also suggested the following improvements to the MDL procedure: (1) Provide clarification to indicate that blank samples can be used to estimate the MDL if those blanks generate a signal; (2) revise the language in Step 1 of the MDL procedure to address certain common misunderstandings (*e.g.*, strengthen the discussion of the selection of the spiking level used for the MDL study); and (3) specify that the spike level used to establish the MDL should not be more than a factor of three times greater than the calculated MDL. The first two suggestions from the peer reviewers regarding improvements to the MDL procedure, have been included in the proposed revision to the MDL procedure. Although EPA agrees with the theoretical arguments related to the last suggestion regarding the spike level, EPA already tested this suggestion in one of its studies of detection and quantitation concepts and found that it could create laboratory burdens that far exceed the benefits. Specifically, EPA required a spike-to-MDL ratio of three in its multi-technique variability studies (the ''Episode 6000 studies''), which are described in the Assessment Document supporting this rule. Two laboratories reported that a large number of iterations would be required (particularly in multiple-analyte methods) in order to achieved a spike-to-MDL ratio of three, and would result in increased laboratory burden and cost. Therefore, this suggestion is not incorporated into the revised MDL procedure in this proposed rule.

Based on peer review comments and comments received over the years from the laboratory community, the Petitioners, and other stakeholders, EPA is proposing revisions to the MDL procedure (see section VII below).

VII. Proposed Revisions to the MDL and ML

This proposal would revise the definition of detection limit for use under the CWA. It also would revise certain aspects of the existing procedure for determining the Method Detection Limit (MDL) in 40 CFR part 136, Appendix B (Definition and Procedure for the Determination of the Method Detection Limit) and modify the discussion to clarify implementation of the procedure. It also requests comment on whether to add a stand-alone definition of quantitation limit and procedure for determining the Minimum Level of Quantitation (ML) in Appendix B.

This proposal incorporates the results of EPA's recent assessment of detection and quantitation concepts and procedures discussed throughout this preamble and in the Assessment Document, and address various stakeholder comments received by EPA since the 1984 promulgation of the MDL (49 FR 43234, October 26, 1984).

The following discussion is divided into five sections: (1) Revisions to the definition of the detection limit are discussed in section VII.A; (2) technical revisions to the MDL procedure are discussed in section VII.B; (3) clarifications and other minor editorial changes to the MDL procedure are discussed in section VII.C; (4) the addition of a definition of quantitation limit and the addition of a procedure to calculate the ML are discussed in section VII.D; (5) section VII.E discusses EPA's continued acceptance of analytical methods from organizations that do not necessarily use EPA's MDL and ML procedures.

A. Definition of the Detection Limit

Section 136.2(f) currently defines the term ''detection limit'' to mean ''the minimum concentration of an analyte (substance) that can be measured and reported with a 99% confidence that the analyte concentration is greater than zero as determined by the procedure set forth at appendix B of this part.'' EPA is proposing to revise § 136.2(f) to explicitly equate the term ''detection limit'' with the ''method detection limit'' and to reflect the proposed revisions to the MDL procedure at Appendix B as follows: ''*Detection limit* means the method detection limit (MDL), as determined by the procedure set forth at Appendix B of this part. The MDL is an estimate of the measured concentration at which there is 99% confidence that a given analyte is present in a given sample matrix.'' EPA also is proposing to revise the definition of the Method Detection Limit included in Appendix B as follows: ''The MDL is an estimate of the measured concentration at which there is 99% confidence that a given analyte is present in a given sample matrix.'' The MDL is the concentration at which a decision is made regarding whether an analyte is detected by a given analytical method. The MDL is calculated from replicate analyses of a matrix containing the analyte and is functionally analogous to the ''critical value'' described by Currie (1968, 1995) and the Limit of Detection described by the American Chemical Society (Keith *et al.*, 1980, McDougal *et al.*, 1983).

EPA also is requesting comment on an alternative approach in which the term *limit of detection* would be defined at § 136.2 as ''the critical value, which is the concentration at which there is 99% confidence that a given analyte is present in a given sample matrix,'' and the *method detection limit* would be defined as ''the procedure set forth in Appendix B of this part, which can be used to estimate the limit of detection (*i.e.*, critical value).''

B. Technical Revisions to the MDL Procedure

This notice proposes several technical revisions to the MDL procedure at 40 CFR part 136, Appendix B. These revisions are based on EPA's recent assessment of detection and quantitation concepts described in the Assessment Document, as well as comments received from stakeholders, the Petitioners, and the peer reviewers of the assessment. Specifically, the proposed revisions would:

1. Revise the definition of the MDL to replace the term ''minimum concentration'' with the term ''estimate of the measured concentration'' and replace the phrase ''greater than zero'' with the phrase ''present in a given sample matrix.'' The revised definition would note the functional analogy of the MDL with the ''critical value'' described by Currie (1968 and 1995) and the ''limit of detection'' (LOD) described by the American Chemical Society in 1980 and 1983. The revised definition also would note that the MDL represents the concentration at which the detection decision is made. These proposed revisions are intended to make the definition of the MDL more consistent with the MDL procedure. The proposed revisions reflect peer review comments on EPA's recent assessment of detection and quantitation concepts and procedures.

2. Expand the Scope and Application discussion to recognize that there are a variety of purposes and analytical methods for which the MDL procedure may be employed. The revised text provides examples of four common uses of the MDL procedure (*i.e.*, demonstrating laboratory capability with a particular method; monitoring trends in laboratory performance; characterizing method sensitivity in a particular matrix; and establishing an MDL for a new or revised method for nationwide use). The revised text also clarifies that the procedure may not be applicable to certain test methods such as those used to measure pH or temperature, for example. These revisions are based on questions from stakeholders about the scope and applicability of the MDL procedure.

3. Revise three of the four considerations for estimating the detection limit (see Step 1 of the current MDL procedure and section 4.3 of the proposed revisions), and suggest that the method-specified MDL can be used as the initial estimate when performing an MDL study to verify laboratory performance or to demonstrate that the MDL can be achieved in a specific matrix. The proposed revisions to the original considerations include: (1) Clarifying that, if analysis of blank samples yields an instrument response, the detection limit can be estimated as approximately equal to three times the standard deviation of replicate measurements of the analyte in the blank; (2) replacing ''that region of the standard curve where there is a significant change in sensitivity (*i.e.*, a break in the slope of the standard curve)'' with ''a concentration in the region of constant or effectively-constant standard deviation at low concentrations;'' and (3) replacing ''instrumental limitations'' with ''the lowest concentration that can be detected by analyzing samples containing successively lower concentrations of the analyte.''

4. Revise the specifications for establishing the test concentration range according to the intended application of the MDL as follows: (1) If verifying a published MDL, the test concentration should be no more than five times the published MDL; (2) if verifying an MDL to support a regulatory objective or the objective of a study or program, the test concentration should be no more than one third the compliance or target limit; (3) if determining an MDL for a new or revised method, the test concentration should be no more than five times the estimated detection limit; and (4) if performing an iteration, the test concentration should be no more than five times the MDL determined in the most recent iteration. (See Step 3.1 of the current procedure and section 4.3.1 of the proposed revisions.)

5. Delete the calculation of a 95% confidence interval estimate for the MDL. EPA has determined that these calculations are neither routinely performed by laboratories, nor are the results employed by regulatory agencies, including EPA.

6. Revise the discussion of the iterative procedure to require that the iterative procedure be used to verify the reasonableness of the MDL when developing an MDL for a new or revised method or when developing a matrix-specific MDL, but that it remain optional when determining an MDL to verify a method-, matrix-, program-, or study-specific MDL. This change recognizes that the iterative procedure is rarely used to verify laboratory performance, but is considered important during method development. The discussion, as revised, also would provide specific instructions on how to assess the reasonableness of an MDL used to verify laboratory performance. (See Step 7 of the current procedure and section 4.8 of the proposed revision.)

7. Add a new section (section 4.9) to the MDL procedure to address the treatment of suspected outliers. EPA is proposing to add this section in response to frequent questions from stakeholders with regard to outliers in the absence of any affirmative statements in the current MDL procedure. The discussion in this proposed section specifies that suspected outliers be examined for spurious errors that may occur as a result of human error or instrument malfunction, recommends that correctable errors be corrected before calculation of the MDL, and requires that any corrective actions be documented. The proposed section specifically would provide for invalidation of results from noncorrectable errors and preclude their use in calculating the MDL. The proposed section also describes the use of the Grubbs test for outlying values as a means to screen the results of the replicate samples for possible outliers, and provides an example application of the Grubbs test. Finally, the proposed section would reiterate the requirement that any results generated from more than seven replicates must be used to calculate the MDL unless they are determined to be outliers by the use of an appropriate outlier test. This proposed change addresses the possibility that some laboratories could prepare more than the requisite seven samples and then select only the seven results that yield the most desirable MDL value. Laboratory auditors from various agencies have identified this practice as a problem that can distort the MDL, but it is not specifically prohibited or addressed in the current procedure.

8. Delete the discussion of analysis and use of blanks included in section 4(a) of the current procedure. The current discussion applies to methods in which a blank measurement is required to calculate the measured level of an analyte; it requires separate measurements of blank samples for each MDL sample aliquot analyzed and subtraction of the average result of the blank samples from each respective MDL sample measurement. The proposed deletion of this discussion is in recognition that subtraction of a single (or average) blank sample result from the result for each MDL sample would not change the standard deviation and thus, would have no effect on the resulting MDL. Although EPA believes laboratories would be prudent to analyze blanks for assessing potential contamination, EPA also believes that requiring analysis of blanks or subtraction of blank results during MDL determinations is unnecessarily burdensome.

9. Revise the optional pre-test described in section 4(b) of the current procedure. The current procedure suggests analyzing two aliquots to evaluate the estimated detection limit before proceeding with the full seven-replicate test. Results from these analyses are evaluated to determine if the sample is in the ''desirable range for determining the MDL,'' but no criteria are provided for establishing this desirable range. The proposed revisions

to the pre-test procedure are intended to address this issue. These revisions now appear in section 4.1 of the proposed procedure. Specifically, the pre-test has been modified to suggest analysis of three aliquots. Results from these analyses are evaluated by calculating a preliminary MDL based on the standard deviation of the analyses, and then determining if this preliminary MDL is within 0.2 to 1.0 times the concentration spiked in the sample. This revision is consistent with the current procedure's recommendation that samples used to determine an MDL contain the analyte at a concentration that is ''between 1 and 5 times the estimated method detection limit.''

C. Editorial Changes to the MDL Procedure

This notice proposes editorial changes to the MDL procedure at 40 CFR part 136, Appendix B that are designed to clarify the existing procedure and improve readability. These editorial changes include changes to the numbering scheme, the addition of clearer titles to some of the procedural steps, and minor clarifications. Specifically, the proposed changes would:

1. Add a summary section to provide an overview of the various steps included in the MDL procedure. The summary section is consistent with the current format for analytical methods and should be particularly helpful to non-laboratory readers.

2. Clarify in the Scope and Application discussion that the MDL procedure is intended for use in EPA's Clean Water Act programs, and that alternative procedures may be used to establish test method sensitivity provided the resulting detection value meets the sensitivity needs for a specific application.

3. Clarify throughout the procedure that not all of the steps are required for every application. This clarification provides consistency with the proposed revisions in the Scope and Application section of the procedure.

4. Expand the discussion of matrix selection to address use of an MDL in either a reference matrix or an alternate matrix. (See Step 2 of the current procedure and section 4.2 of the proposed revisions.) Use of matrices other than reagent water are not discussed until Step 3b of the current procedure. The expanded discussion is intended to provide additional clarity and consistency with the description of the four applications added to the MDL Scope and Application section (see section VII.B.2 above).

5. Expand the discussion of establishing the test concentration range to more clearly describe the steps required and prepare the test samples. (See Step 3 of the current procedure and section 4.3 of the proposed revisions.) These proposed changes are editorial and describe the process that may be used for determining a matrix-specific MDL as well as determining an MDL in a reference matrix such as reagent water. Additional clarifications include recognition that some analytes may require that seven aliquots be prepared individually, as opposed to preparing a bulk sample of sufficient volume to be split into seven aliquots. EPA is proposing this clarification in response to questions from laboratories regarding the appropriate means for preparing the MDL aliquots.

6. Expand the discussion of performing the analyses to include a brief introduction clarifying that the samples used for MDL analyses must be processed using the sample handling, processing, and result calculations specified in the analytical method. (See Step 4 of the current procedure and section 4.4 of the proposed revisions.) This proposed change includes moving this statement from the Reporting section of the current procedure to the more appropriate location in section 4 of the revised procedure. This proposed change also would clarify that blank-correction or recovery-correction procedures are applied to the MDL analyses only when those procedures are employed for routine sample analyses, and precludes their use if they are not specified in the test method. EPA is proposing these changes in response to questions raised by laboratories, the Petitioners, and as a result of the recent assessment.

7. Reorganize the procedural steps contained in Step 4 of the current procedure, such that the optional pre-test of the MDL is discussed before the procedure for performing the full seven-replicate test. (See section 4.4 of the proposed revisions.) EPA is proposing this change strictly to improve ease of use.

8. Expand and reorganize the description of the seven-replicate version of the MDL described in Step 4(a) of the current procedure. The revised version would appear in section 4.5 and reflects comments from stakeholders that the discussion in the current procedure is not sufficiently clear. The revised procedure also would state explicitly that all analytical results must be positive numbers, and that the results from all aliquots analyzed must be used in the calculations, except those identified as outliers using the procedures described in section 4.9 of the revised procedure (see the discussion regarding outliers in VII.B above). These proposed changes would clarify stakeholder concerns regarding those analytical methods (e.g., for metals) that may produce negative numbers at very low concentrations and would emphasize the revision made in response to concerns regarding inappropriate screening of results used for MDL determinations.

9. Simplify the calculations of standard deviation of replicate measurements in Step 5 of the current procedure. (See section 4.6 of the proposed revisions.) For example, the current procedure details the calculation of the sample variance (s^2), and then details the calculation of the sample standard deviation (s) in a separate equation. Given that the variance term does not factor into the MDL calculation directly, the proposed revision would require only calculation of the standard deviation. The proposed revision also would include a caution warning the reader to calculate the sample standard deviation (s), not the population standard deviation (sigma), when using automated programs such as spreadsheets. This error was not as likely to occur in 1984, prior to the ready availability of personal computers and laboratory data systems, but is commonly seen today.

10. Move the table of Student's *t*-values from its current location following the text in Step 7 to section 4.7, where the *t*-value is employed. EPA is proposing this change to improve ease of use and increase readability.

11. Add a table of F-statistic values to the iterative procedure described in section 4.8. EPA is proposing this change to improve ease of use and address those instances in which an iterative MDL might be determined from other than seven replicates per data set.

12. Delete the ''Reporting'' section of the MDL procedure. The existing procedure includes a section listing the information that must be provided with the MDL for each analyte. EPA is proposing to delete this section because it is not relevant to the procedure and it is generally duplicative of reporting and recordkeeping requirements that States, other regulatory entities, or laboratory certification officials already require.

D. Definition and Procedure for Determining the Minimum Level of Quantitation

Although ML values for analytes were published in 1984 in EPA Methods 1624 and 1625 (49 FR 43234, October 26, 1984), the definition of the ML was

provided in a footnote to the tables within those methods. The original definition was intended to define a minimum level of quantitation for these isotope dilution GC/MS methods. However, as described in the Assessment Document, EPA has changed the definition of the ML over the years and has expanded its applicability to other 40 CFR part 136 methods. This proposal requests comment on whether to add the following definition of the ML to Appendix B of 40 CFR part 136: '' the lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point for the analyte, as determined by the procedure set forth at Appendix B of this part. The ML represents the lowest concentration at which an analyte can be measured with a known level of confidence.'' In addition to the definition, EPA requests comment on whether Appendix B should contain an explicit explanation of the calculation of the ML from an MDL value determined using the revised MDL procedure, including a table of multiplier values that may be used when the MDL value is calculated from other than seven replicate analyses.

An alternative is to not incorporate a definition in § 136.2 but to continue to specify the ML on a method-by-method basis. In this case, the ML may continue to be determined and supported with data gathered during method validation studies. This approach would allow maximum flexibility to design studies that are appropriate for the intended use of the method.

A second alternative is to incorporate into § 136.2 the definition of limit of quantitation as ''The lowest concentration of an analyte that can be measured with a defined level of confidence'' and to incorporate the definition of ML (minimum level) as ''The procedure set forth in Appendix B of this part of the same name, which can be used to estimate the limit of quantitation.''

In this proposal, EPA is also requesting comment on whether it should encourage or require that laboratories periodically demonstrate target analyte recovery at the ML by preparing and analyzing a reference matrix sample spiked at the ML using all sample handling and processing steps described in the method. EPA recognizes that existing methods do not provide acceptance criteria for such ''ML standards.'' Therefore, EPA suggests that, if the method does not provide acceptance criteria for an ML standard, acceptance criteria for other spiked reference matrix samples (e.g., laboratory control samples, laboratory fortified blanks, ongoing precision and recovery samples, etc.) may be used to evaluate analyte recovery at the ML. EPA is soliciting comment on whether this recommendation should be made into a mandatory requirement, retained as a recommendation, or replaced by an alternative recommendation for demonstrating recovery at the ML.

E. Acceptance of Test Methods Employing Alternative Detection and Quantitation Procedures

This proposed rule would allow use of alternative detection and quantitation procedures to establish detection and quantitation limits in an analytical method, provided that the resulting detection and quantitation limits meet the sensitivity needs for the specific application. The use of detection and quantitation approaches from voluntary consensus standards bodies (VCSBs) and other organizations is encouraged under the National Technology Transfer and Advancement Act (NTTAA), because it facilitates the approval of analytical methods from these organizations at 40 CFR part 136 without requiring that these organizations specifically employ EPA's MDL and ML procedures to establish method sensitivity. This allowance would result in greater flexibility to establish or improve the sensitivity of methods for use under the Clean Water Act. It also would facilitate approval of analytical methods from VCSBs and other organizations. In selecting an appropriate test method for a specific purpose, the laboratory must always consider the sensitivity of the approved test methods. Only those test methods with the desired sensitivity should be used to meet the objective of the CWA ''to restore and maintain the chemical, physical, and biological integrity of the Nation's waters.''

EPA recognizes that there are alternative detection and quantitation approaches that may be used for determining test method sensitivity. EPA has included test methods at 40 CFR part 136 that employ alternative approaches, although some of these approaches have not been rigorously defined. In its recent assessment of detection and quantitation approaches, EPA evaluated the interlaboratory detection estimate (IDE) and the interlaboratory quantitation estimate (IQE) procedures published by ASTM International. However, EPA is not aware at this time of any published test methods from any source that include specific values for the IDE and the IQE, including test methods published by ASTM International. EPA will consider test methods that include these procedures for use in CWA programs when such methods are available. If ASTM International is successful in developing single-laboratory adaptations of the IDE and IQE that may be used to verify the ability of a given laboratory to achieve the IDE and IQE, then EPA also may consider those single-laboratory approaches in evaluating both method and laboratory performance.

VIII. Industry Proposal

On December 27, 2002, the Inter-Industry Analytical Group (IIAG) submitted a proposal that recommends (1) a sensitivity test intended to ''replace the MDL as a test of whether an individual laboratory is performing adequately,'' and (2) an interlaboratory validation study design intended to characterize precision and accuracy of methods used for regulatory compliance. EPA did not have the opportunity to evaluate IIAG's proposal against the criteria discussed in Section IV of this preamble, but intends to do so prior to publication of a final rule. EPA is providing a summary of the recommendations contained in the ''Inter-Industry Analytical Group Proposal for Sensitivity Test and Full-Range Interlaboratory Validation Study'' here. The complete text of the recommendations has been placed in the docket supporting this proposed rule. EPA is soliciting comment on the industry recommendations.

IIAG is proposing a sensitivity test in place of the MDL for determining laboratory performance capability. The proposed sensitivity test includes the provision that EPA first determine the lowest calibration point of a method, prescribe a dilution of that calibration point as the spike level (e.g., at one-half or two-thirds the lowest calibration point), specify a required number of replicates, and set a quality control acceptance criterion. IIAG asserts that an advantage of such a test is that it would provide all laboratories with a single spike level and an ''unambiguous pass or no-pass test.'' EPA is soliciting comment on approaches that might be considered appropriate for such determinations (i.e., the lowest calibration point of a method, an appropriate dilution, a number of replicates, and an acceptance criterion for standard deviation between measurements of the replicates). EPA also is soliciting comment on how IIAG's recommended sensitivity test would be either more appropriate or less appropriate than either the current MDL and ML procedures or the MDL and ML

procedures if revised according to this proposed rule.

IIAG's proposed ''full range'' validation study is intended to determine precision and bias across the entire working range of an analytical method (*i.e.,* from a blank to the upper end of the working range) and would account for variability between laboratories. IIAG recommends that, unlike the MDL and IIAG's proposed sensitivity test, the ''full-range'' validation study could be used to characterize bias and precision across the entire working range of the method and results of such a study could be used to establish an interlaboratory method detection level. EPA is requesting comment on the use of data generated through a ''full range'' validation study to determine a quantitation level, detection level, and corresponding bias and precision criteria that are applicable throughout the entire working range of the method. EPA also is soliciting comment on how IIAG's recommended ''full range'' validation study would be either more appropriate or less appropriate than EPA's use of interlaboratory validation studies, which are designed in accordance with ASTM Standard D 2777, or other appropriate standards. For example, EPA used the ASTM standard to validate EPA Method 1631 (see Interlaboratory Validation Study of EPA Method 1631).

IX. Solicitation of Comments

EPA is hereby requesting public comment on the proposed revisions discussed in section VII of this preamble and on the industry proposal discussed in section VIII. Specifically, EPA is requesting comment on the proposed revisions to the Definition and Procedure for the Determination of the Method Detection Limit at 40 CFR part 136 (Appendix B), to the proposed revision to the definition of ''Detection Limit,'' on whether EPA should add definition of ''Minimum Level'' at 40 CFR 136.2, and on whether and how the sensitivity test described in the industry proposal could be used in CWA programs. EPA is also requesting public comment on the Assessment Document supporting the proposed revisions discussed in this notice elsewhere in today's **Federal Register** (see Notice of Document Availability and Public Comment Period for the Technical Support Document for the Assessment of Detection and Quantitation Concepts).

Commenters are encouraged to support their views with data or information that would assist EPA in making a final decision on detection and quantitation procedures for EPA's CWA applications. To ensure that EPA can properly respond to comments, commenters should cite, where possible, the paragraph(s) or section(s) in this proposal to which each comment refers. For further details on submission of comments, please see the **DATES; ADDRESSES;** and ''How to Submit Comments'' sections at the beginning of this preamble.

EPA is particularly requesting comment on the following:

1. EPA is requesting comment on whether to include a definition and procedure for the ML in Appendix B of 40 CFR part 136 (see section VII.D of this preamble). EPA is soliciting comment on whether the proposed addition of an ML definition and procedure in Appendix B is appropriate, or whether either of the alternatives discussed in section VII.D are more appropriate to maintain flexibility in the application of different quantitation approaches.

2. EPA is proposing a recommendation that laboratories periodically demonstrate target analyte recovery at the ML by preparing and analyzing a reference matrix sample spiked at the ML (see section VII.D of this preamble). Specifically, EPA is soliciting comment on whether this recommendation should be made into a mandatory requirement, retained as a recommendation, or replaced by an alternative recommendation for demonstrating recovery at the ML. EPA also is soliciting comments and recommendations regarding procedures for establishing acceptance criteria for ML recovery, and when application of the criteria would be appropriate (*e.g.*, development of new methods, validation of data), if such a requirement were mandatory.

3. EPA is proposing to add a new Step 8 to the MDL procedure to address the identification and treatment of suspected outliers (see Section VII.B.7 of this preamble). This proposed step includes provision for invalidation of results from noncorrectable errors and precludes their use in calculating the MDL. The proposed step also states: ''Given the small number of replicates typically used to determine the MDL, it is inappropriate to use a data set that contains more than one statistical outlier.'' EPA requests comment on (1) the procedures for identifying outliers, (2) the specification that only one outlier may be removed from a data set that is used for MDL determination, and (3) the appropriateness of allowing use of a data set containing six results if an outlier is identified and removed from a data set containing results from the required minimum of seven replicate samples.

4. EPA is proposing to revise the specifications for establishing the test concentration (spike level) that will be used in the determining the MDL according to the intended application of the MDL (see Section VII.A.4 of this preamble). EPA is soliciting comment on these levels and on the appropriateness of applying these levels according to the intended use of the MDL.

5. EPA is soliciting comment on the sensitivity test and ''full-range'' validation study described by IIAG and included in the public docket supporting this proposed rule (see Section VII of this preamble). EPA is specifically soliciting comment on those aspects of IIAG's proposed study that relate to detection and quantitation issues.

6. EPA is proposing to delete the Reporting section of the existing MDL procedure. EPA is soliciting comments on whether this change is appropriate.

X. Statutory and Executive Order Reviews

A. Executive Order 12866: Regulatory Planning and Review

Under Executive Order 12866 (58 FR 51735 (October 4, 1993)), the Agency must determine whether the regulatory action is ''significant'' and therefore subject to Office of Management and Budget (OMB) review and the requirements of the Executive Order. The Executive Order defines ''significant regulatory action'' as one that is likely to result in a rule that may:

(1) Have an annual effect on the economy of $100 million or more, or adversely affect in a material way the economy, a sector of the economy, productivity, competition, jobs, the environment, public health or safety, or State, local, or Tribal governments or communities;

(2) Create a serious inconsistency or otherwise interfere with an action taken or planned by another agency;

(3) Materially alter the budgetary impact of entitlements, grants, user fees, or loan programs or the rights and obligations of recipients thereof; or

(4) Raise novel legal or policy issues arising out of legal mandates, the President's priorities, or the principles set forth in the Executive Order.

It has been determined that this rule is not a ''significant regulatory action'' under the terms of Executive Order 12866 and is therefore not subject to OMB review.

B. Paperwork Reduction Act

This action does not impose an information collection burden under the provisions of the Paperwork Reduction Act, 44 U.S.C. 3501 *et seq*. This action imposes no information collection, reporting or recordkeeping requirements. Burden means the total time, effort, or financial resources expended by persons to generate, maintain, retain, or disclose or provide information to or for a Federal agency. This includes the time needed to review instructions; develop, acquire, install, and utilize technology and systems for the purposes of collecting, validating, and verifying information, processing and maintaining information, and disclosing and providing information; adjust the existing ways to comply with any previously applicable instructions and requirements; train personnel to be able to respond to a collection of information; search data sources; complete and review the collection of information; and transmit or otherwise disclose the information.

An Agency may not conduct or sponsor, and a person is not required to respond to a collection of information, unless it displays a currently valid OMB control number. The OMB control numbers for EPA's regulations are listed in 40 CFR part 9 and 48 CFR chapter 15.

C. Regulatory Flexibility Act

The Regulatory Flexibility Act (RFA) generally requires an agency to prepare a regulatory flexibility analysis of any rule subject to notice and comment rulemaking requirements under the Administrative Procedure Act or any other statute unless the agency certifies that the rule will not have a significant economic impact on a substantial number of small entities. Small entities include small businesses, small organizations, and small governmental jurisdictions.

For purposes of assessing the impacts of this rule on small entities, small entity is defined as: (1) A small business as defined by the U.S. Small Business Administration definitions at 13 CFR 121.201; (2) a small governmental jurisdiction that is a government of a city, county, town, school district or special district with a population of less than 50,000; and (3) a small organization that is any not-for-profit enterprise which is independently owned and operated and is not dominant in its field.

After considering the economic impacts of this proposed rule on small entities, I certify that this action will not have a significant economic impact on a substantial number of small entities. This rule proposes to modify existing procedures in 40 CFR part 136, appendix B for determination of detection and quantitation in analytical methods. This modification would clarify and improve existing procedures.

Overall, the costs of this modification are minimal. Many laboratories using analytical test methods are already implementing aspects of the modification, further minimizing any potential cost increases. Therefore, EPA believes that this rule will not have a significant economic impact on a substantial number of small entities. We continue to be interested in the potential impacts of the proposed rule on small entities and welcome comments on issues related to such impacts.

D. Unfunded Mandates Reform Act

Title II of the Unfunded Mandates Reform Act of 1995 (UMRA), Public Law 104–4, establishes requirements for Federal agencies to assess the effects of their regulatory actions on State, Tribal, and local governments and the private sector. Under section 202 of the UMRA, EPA generally must prepare a written statement, including a cost-benefit analysis, for proposed and final rules with ''Federal mandates'' that may result in expenditures to State, Tribal, and local governments, in the aggregate, or to the private sector, of $100 million or more in any one year. Before promulgating an EPA rule for which a written statement is needed, section 205 of the UMRA generally requires EPA to identify and consider a reasonable number of regulatory alternatives and adopt the least costly, most cost-effective or least burdensome alternative that achieves the objectives of the rule. The provisions of section 205 do not apply when they are inconsistent with applicable law. Moreover, section 205 allows EPA to adopt an alternative other than the least costly, most cost-effective or least burdensome alternative if the Administrator publishes with the final rule an explanation of why that alternative was not adopted.

Before EPA establishes any regulatory requirements that may significantly or uniquely affect small governments, including Tribal governments, it must have developed under section 203 of the UMRA a small government agency plan. The plan must provide for the notification of potentially affected small governments, enabling officials of affected small governments to have meaningful and timely input in the development of EPA regulatory proposals with significant Federal intergovernmental mandates, and informing, educating, and advising small governments on compliance with the regulatory requirements.

This proposed rule contains no Federal mandate (under the regulatory provisions of Title II of the UMRA) for State, Tribal, and local governments or the private sector in any one year. This rule imposes no enforceable duty on any State, local, or Tribal governments or the private sector. This rule proposes to modify existing procedures in 40 CFR part 136, appendix B for determination of detection and quantitation in analytical methods. This modification would clarify and improve current procedures. Overall, the costs of this modification are minimal. Thus, this rule is not subject to sections 202 and 205 of the UMRA. For the same reasons, EPA has also determined that this rule contains no regulatory requirements that might significantly or uniquely affect small governments. Thus, this rule also is not subject to the requirements of section 203 of the UMRA.

E. Executive Order 13132: Federalism

Executive Order 13132, entitled ''Federalism'' (64 FR 43255, August 10, 1999), requires EPA to develop an accountable process to ensure ''meaningful and timely input by State and local officials in the development of regulatory policies that have federalism implications.'' ''Policies that have federalism implications'' is defined in the Executive Order to include regulations that have ''substantial direct effects on the States, on the relationship between the national government and the States, or on the distribution of power and responsibilities among the various levels of government.''

This proposed rule does not have federalism implications. It will not have substantial direct effects on the States, on the relationship between the national government and the States, or on the distribution of power and responsibilities among the various levels of government, as specified in Executive Order 13132. This rule proposes to modify existing procedures in 40 CFR part 136, Appendix B for determination of detection and quantitation in analytical methods. This modification would clarify and improve existing procedures. The costs of this rule for State and local governments are minimal. Thus, Executive Order 13132 does not apply to this rule. In the spirit of Executive Order 13132, and consistent with EPA policy to promote communications between EPA and State and local governments, EPA specifically solicits comments on this proposed rule from State and local officials.

F. Executive Order 13175: Consultation and Coordination with Indian Tribal Governments

Executive Order 13175, titled ''Consultation and Coordination With Indian Tribal Governments'' (65 FR 67249, November 9, 2000), requires EPA to develop an accountable process to ensure ''meaningful and timely input by Tribal officials in the development of regulatory policies that have Tribal implications.'' ''Policies that have Tribal implications'' is defined in the Executive Order to include regulations that have ''substantial direct effects on one or more Indian Tribes, on the relationship between the Federal government and the Indian Tribes, or on the distribution of power and responsibilities between the Federal government and Indian Tribes.''

This proposed rule does not have Tribal implications. It will not have substantial direct effects on Tribal governments, on the relationship between the Federal government and Indian Tribes, or on the distribution of power and responsibilities between the Federal government and Indian Tribes, as specified in Executive Order 13175. This rule proposes to modify existing procedures in 40 CFR part 136, Appendix B for determination of detection and quantitation in analytical methods. This modification would clarify and improve existing procedures. The costs of this rule for Tribal governments are minimal. Thus, Executive Order 13175 does not apply to this rule. In the spirit of Executive Order 13175, and consistent with EPA policy to promote communications between EPA and Tribal governments, EPA specifically solicits comments on this proposed rule from Tribal officials.

G. Executive Order 13045: Protection of Children From Environmental Health & Safety Risks

Executive Order 13045 (62 FR 19885, April 23, 1997) applies to any rule that: (1) Is determined to be ''economically significant'' as defined under Executive Order 12866, and (2) concerns an environmental health or safety risk that EPA has reason to believe may have a disproportionate effect on children. If the regulatory action meets both criteria, the Agency must evaluate the environmental health or safety effects of the planned rule on children, and explain why the planned regulation is preferable to other potentially effective and reasonably feasible alternatives considered by the Agency. This proposed rule is not subject to Executive Order 13045 because it is not ''economically significant'' as defined in Executive Order 12866. Furthermore, it does not concern an environmental health or safety risk that EPA has reason to believe may have a disproportionate effect on children.

H. Executive Order 13211: Actions That Significantly Affect Energy Supply, Distribution, or Use

This rule is not subject to Executive Order 13211, ''Actions Concerning Regulations That Significantly Affect Energy Supply, Distribution, or Use'' (66 FR 28355 (May 22, 2001)) because it is not a significant regulatory action under Executive Order 12866.

I. National Technology Transfer and Advancement Act

Section 12(d) of the National Technology Transfer and Advancement Act of 1995, (''NTTAA''), Public Law 104–113, section 12(d) (15 U.S.C. 272 note), directs EPA to use voluntary consensus standards in its regulatory activities unless to do so would be inconsistent with applicable law or otherwise impractical. Voluntary consensus standards are technical standards (*e.g.,* material specifications, test methods, sampling procedures, business practices) that are developed or adopted by voluntary consensus standard bodies. The NTTAA directs EPA to provide Congress, through the Office of Management and Budget (OMB), explanations when the Agency decides not to use available and applicable voluntary consensus standards.

This proposed rulemaking involves technical standards. Therefore, the Agency identified and evaluated potential voluntary consensus standards. Specifically, EPA identified and evaluated potential detection and quantitation concepts and procedures published by the American Society for Testing and Materials (ASTM International), from the International Organization for Standardization (ISO), the International Union of Pure and Applied Chemistry (IUPAC), and the American Chemical Society (ACS). EPA determined that, although ISO, IUPAC, and ACS have published terms and definitions for detection and quantitation, these organizations have not published an applicable standard (*i.e.,* a step-by-step protocol to make a detection or quantitation determination). EPA did identify applicable standards from ASTM International (the IDE and IQE). This proposed rulemaking would allow the use of these procedures for methods development purposes and would allow the use of any analytical methods with an IDE and IQE, provided these test methods meet the analytical sensitivity requirements for a specific data use. There is currently no applicable voluntary consensus standard for detection and quantitation for laboratory quality control purposes. EPA welcomes comments on this aspect of the proposed rulemaking and, specifically, invites the public to identify potentially applicable voluntary consensus standards and to explain why such standards should be used in this regulation.

XI. References

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Appendix A: Definitions, Acronyms, and Abbreviations Used in This Document

AAMA—American Automobile Manufacturers Association
ACS—American Chemical Society
AOAC—Association of Official Analytical Chemists (now AOAC-International)
APHA—American Public Health Association
ASTM—American Society for Testing and Materials (now ASTM International)
ATP—Alternate Test Procedure
AWWA—American Water Works Association
CBI—confidential business information
CFR—Code of Federal Regulations
CRV—critical value
CWA—Clean Water Act—Federal Water Pollution Control Act Amendments (33 U.S.C. 1251 *et seq.*)
EPA—Environmental Protection Agency
EPRI—Electric Power Research Institute
FR—**Federal Register**

IDE—interlaboratory detection estimate
IIAG—Inter-Industry Analytical Group
IQE—interlaboratory quantitation estimate
ISO—International Organization for Standardization
IUPAC—International Union of Pure and Applied Chemistry
LOD—limit of detection
LOQ—limit of quantitation
MDL—method detection limit
MDV—minimum detectable value
ML—minimum level of quantitation
NBS—National Bureau of Standards (now NIST)
NIST—National Institute of Standards and Technology (formerly NBS)
NPDES—National pollutant discharge elimination system
NTTAA—National Technology Transfer and Advancement Act
OMB—Office of Management and Budget
POTW—Publicly-owned treatment works
RFA—Regulatory Flexibility Act
SBREFA—Small Business Regulatory Enforcement Fairness Act
SCC—Sample Control Center
TSD—technical support document
UMRA—Unfunded Mandates Reform Act
USATHAMA—U.S. Army Toxic and Hazardous Materials Agency (now the U.S. Army Environmental Center [USAEC])
U.S.C.—United States Code
WQBEL—water-quality-based effluent limit
WEF—Water Environment Federation

List of Subjects at 40 CFR Part 136

Environmental protection, Reporting and recordkeeping requirements, Water pollution control.

Dated: February 28, 2003.

Christine Todd Whitman,

Administrator.

For the reasons set out in the preamble, title 40, chapter I of the Code of Federal Regulations, is proposed to be amended as follows:

PART 136—GUIDELINES ESTABLISHING TEST PROCEDURES FOR THE ANALYSIS OF POLLUTANTS

1. The authority citation for part 136 continues to read as follows:

Authority: Secs. 301, 304(h), 307, and 501(a), Pub. L. 95–217, 91 Stat. 1566, *et seq.* (33 U.S.C. 1251, *et seq.*) (The Federal Water Pollution Control Act Amendments of 1972 as amended by the Clean Water Act of 1977).

2. Section 136.2 is amended by revising paragraph (f) and adding paragraph (g) to read as follows:

§ 136.2 Definitions.

* * * * *

(f) Detection limit means the method detection limit (MDL), as determined by the procedure set forth at Appendix B of this part. The MDL is an estimate of the measured concentration at which there is 99% confidence that a given analyte is present in a given sample matrix.

(g) Minimum level of quantitation (ML) means the lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point for the analyte, as determined by the procedure set forth at Appendix B of this part. The ML represents the lowest concentration at which an analyte can be measured with a known level of confidence.

3. Appendix B of part 136 is revised to read as follows:

Appendix B to Part 136

A. Definition and Procedure for the Determination of the Method Detection Limit—Revision 2

1.0 Definition

The method detection limit (MDL) is an estimate of the measured concentration at which there is 99% confidence that a given analyte is present in a given sample matrix. The MDL is the concentration at which a decision is made regarding whether an analyte is detected by a given analytical method. The MDL is calculated from replicate analyses of a matrix containing the analyte and is functionally analogous to the ''critical value'' described by Currie (1968, 1995) and the Limit of Detection (LOD) described by the American Chemical Society (Keith et al., 1980, McDougal et al., 1983).

2.0 Scope and Application

2.1 This procedure is for the determination of an MDL for a given analyte (parameter) in a given matrix (the component or substrate that contains the analyte) using a given test procedure (analytical method). It is applicable to a wide variety of analytes, matrices, and instruments, and to a broad variety of physical and chemical analytical methods, with some exceptions (e.g., pH, temperature). This procedure is intended for use in EPA's Clean Water Act (CWA) programs. An alternative procedure may be used (e.g., from a voluntary consensus standards body) to establish the sensitivity of an analytical method, provided the resulting detection limit meets the sensitivity needs for the specific application.

2.2 This procedure requires a complete, specific, and well-defined analytical method. It is essential that all sample processing steps of the analytical method that are applied to routine analyses be included in determination of an MDL.

2.3 This procedure may be used for a variety of applications, including, but not limited to:

2.3.1 Demonstrating laboratory capability with a particular method. A laboratory using this procedure to demonstrate capability with a particular method is not required to perform the iterative verification of the MDL (section 4.8) if the laboratory-determined MDL is less than or equal to either the MDL in the method, the MDL required to support a regulation, or the objectives of a study (see section 4.8.5).

2.3.2 Monitoring trends in laboratory performance. When used in this manner, the MDL for a given analyte measured using a given analytical method may vary as a function of laboratory experience and the matrix tested.

2.3.3 Characterizing method sensitivity in a particular matrix. An MDL is typically determined in a reference matrix. However, it also may be determined in a real-world matrix to verify that the target MDL can be achieved in that matrix.

2.3.3.1 If the MDL required for a specific application can be achieved in a real-world matrix, that MDL may be used in lieu of a reference-matrix MDL, and iteration (section 4.8) is not necessary.

2.3.3.2 If the MDL needed for a specific application cannot be achieved in the real-world matrix (i.e., if the purpose of the MDL study is to demonstrate the effects of matrix interferences in a real world sample), the laboratory must (1) perform an MDL study in a reference matrix to demonstrate the laboratory's ability to apply the method in the absence of interferences, and (2) verify the matrix-specific MDL through the iterative procedure given in section 4.8.

2.3.3.3 Refer to section 4.2 for additional information concerning the selection of test matrices.

2.3.4 Establishing an MDL for a new or revised method for nationwide use. When the procedure is used to establish an MDL for a new or revised method, the MDL should be derived from data obtained from multiple laboratories. Organizations developing or revising methods must document and make available the data and procedures used to establish an MDL to obtain approval for use under Clean Water Act programs.

3.0 Summary of the Procedure

3.1 The procedural steps required for determining an MDL vary with the intended application of the MDL. However, regardless of the intended application, all MDL determinations must include the following steps:

(a) Estimating the detection limit of the method as practiced,

(b) Selecting the appropriate matrix to be used in the determination,

(c) Selecting the appropriate test concentration,

(d) Preparing and analyzing a minimum of seven replicate aliquots of a blank or spiked matrix,

(e) Calculating the mean concentration of the analyte, the standard deviation of that mean, and the MDL, using the formula provided in this procedure,

(f) Comparing the calculated MDL to a method-specified MDL, relevant regulatory requirements, or project-specific objectives, as appropriate.

3.2 When developing MDLs for new or revised methods, or developing matrix-specific MDLs for nationwide use, the procedure also may include:

(a) Conducting an optional pre-test using fewer replicates to verify that an appropriate

concentration was selected to perform the MDL test,

(b) Conducting an iterative procedure involving analyses of additional replicates to verify the reasonableness of the MDL (required for method development),

(c) Determining the MDL in additional relevant matrices or in multiple laboratories.

4.0 Procedure

4.1 Estimate the detection limit of the method

If the purpose of determining the MDL is to verify laboratory performance using a specific method or to determine the MDL in a specific matrix, the laboratory should use the MDL published in the method as the initial estimate. If the MDL is being determined for other reasons (e.g., method development), the experience of the laboratory is important to properly estimate the detection limit. The laboratory must include at least one of the following considerations in producing this initial estimate:

4.1.1 The concentration of analyte that produces an instrument signal/noise in the range of 2.5 to 5 for those instances in which an instrument is used for the determination.

4.1.2 The concentration approximately equal to three times the standard deviation of replicate measurements of the analyte in a blank. If analysis of the blank produces no response (zero), use the concentration approximately equal to three times the standard deviation of replicate measurements at the lowest concentration that always produces a response.

4.1.3 A concentration in the region of constant or effectively constant standard deviation at low concentrations. This assumes that the model of Glaser et al. (1981), which includes a low concentration region where the standard deviation of the measurement error is constant or effectively constant, is suitable to describe the measurement process for the analytical method under consideration.

4.1.4 The lowest concentration that can be detected by analyzing samples containing successively lower concentrations of the analyte.

4.2 Select the matrix to be used to develop the MDL. The MDL is typically determined in a reference matrix. However, it may be determined in a real-world matrix to verify that the MDL required for a specific application can be achieved in that matrix.

4.2.1 Reference Matrix

The most common reference matrix is reagent water. Reagent water is defined as water in which the analyte and interferences are not detected at the MDL or, if this is the initial estimate, detected at the detection limit estimated in section 4.1. An interference is defined as a systematic error in the measured analytical signal caused by the presence of a substance other than the analyte. Other common reference matrices are sand as a reference matrix for soils, sediments, and other solid samples; and corn oil as a reference matrix for tissue samples. After selecting the reference matrix to be tested, proceed to section 4.3.

4.2.2 Matrices other than a reference matrix

4.2.2.1 If the MDL determined in a matrix other than a reference matrix is sufficient to meet requirements of the specific application (e.g., the laboratory is able to meet the MDL required for compliance monitoring or published in the method), it is not necessary to determine the MDL in a reference matrix.

4.2.2.2 If the purpose of a matrix-specific MDL is to determine the effects of matrix interferences in a real-world sample, the laboratory also must determine the MDL in a reference matrix to demonstrate the laboratory's ability to apply the method in the absence of interferences.

Note to Section 4.2.2.2: A laboratory seeking to develop a matrix-specific MDL for a specific method must use the same cleanup steps that will be used for analysis of samples.

4.3 Establish the test concentration range and prepare test samples Establish the test concentration range per section 4.3.1. Prepare the test samples from a reference matrix per section 4.3.2, or from an alternative matrix per section 4.3.3. Prepare a sufficient quantity of the matrix to provide samples for a minimum of seven analyses.

Note to Section 4.3: For analytes for which a single-volume (bulk) sample or spiked single-volume sample would result in non-homogenous replicates (e.g., for determination of ''oil and grease''), or for which preparation of a spiked single-volume sample is impractical, a minimum of seven individual aliquots should be prepared at the test concentration.

4.3.1 Establish the test concentration range as follows.

4.3.1.1 If verifying an MDL that is published in an analytical method, the test concentration should be no more than five times the published MDL.

4.3.1.2 If verifying an MDL required to support a regulatory objective or the objective of a specific study or program, the test concentration should be no more than one third the compliance or target limit.

4.3.1.3 If performing an MDL study for a new or revised method, the test concentration should be no more than five times the detection limit estimated in section 4.1.

4.3.1.4 If performing an iteration (see section 4.8), the test concentration should be no more than five times the MDL determined in the most recent iteration.

4.3.2 Preparing test samples from a reference matrix

If a blank sample produces an acceptable signal (see section 4.3.2), spiking is not required; otherwise, spike the reference matrix at the concentration established in section 4.3.1. Proceed to section 4.4.

Note to Section 4.3.2: The laboratory must ensure that the levels in blanks are not too high. Otherwise, the resulting MDL produced may be artificially biased. For a spiked sample, the concentration of the contaminant in the blank should not be a significant portion of the total concentration since this also could result in an artificial bias for the MDL. It is important to spike the analyte at the proper concentration (section 4.3) to ensure the MDL is determined accurately.

4.3.3 Preparing test samples from a matrix other than a reference matrix

Analyze three aliquots of the sample matrix to characterize the concentration of the target analyte(s) present in the matrix.

4.3.3.1 If the average measured concentration of the analyte in the matrix is less than five times the concentration established in section 4.3.1, proceed to section 4.4.

4.3.3.2 If the average measured concentration of the analyte in the matrix is less than the concentration range established in section 4.3.1, spike the matrix to bring the concentration of the analyte to the established concentration range and proceed to section 4.4.

4.3.3.3 If the average measured concentration of the analyte in the matrix is greater than the concentration range established in section 4.3.1, reduce the concentration of the analyte to the established concentration range, using one of the following techniques before proceeding to section 4.4:

4.3.3.3.1 Selectively remove the analyte from the matrix.

4.3.3.3.2 Obtain another matrix with a lower concentration of the analyte.

4.3.3.3.3 Dilute a sample of the matrix with the appropriate reference matrix. For example, if the matrix is aqueous, dilute the sample with reagent water.

Note to Section 4.3.3.3.3: Dilution should be used only if the analyte cannot be selectively removed (3.3.3.1) or if another matrix with a lower analyte concentration cannot be obtained (3.3.3.2) because dilution of the sample has the potential to dilute any interferences present.

4.4 Perform the analyses

4.4.1 The analyses in section 4.4.3 (optional pre-test of estimated detection limit) and 4.2 (MDL analyses) must be performed using all of the routinely employed calibration, sample handling, processing, and result calculations specified in the analytical method. For example, many methods contain multiple sample cleanup options; any and all cleanup options routinely used to analyze a sample must be used when analyzing the replicate samples prepared in section 4.3.

4.4.2 Similarly, if the analytical method employs recovery-correction or blank-correction procedures for calculating results, those procedures must be used when calculating results of an analysis of each aliquot. If a recovery- or blank-correction procedure is not specified in the test method, such correction must not be used.

4.4.3 Optional pre-test

It may be economically and technically desirable to evaluate the estimate of the detection limit (section 4.1) before proceeding with determination of the MDL in section 4.5. This pre-test attempts to ensure that the MDL study is being conducted at the correct concentration to prevent repeating the entire study; it may be particularly useful when the analytical costs are high. To evaluate the estimated detection limit, proceed as follows:

4.4.3.1 Process three aliquots of the test sample prepared in section 4.3 through the entire method, per section 4.5.

4.4.3.2 Calculate the standard deviation of results for the three aliquots as follows:

$$s = \sqrt{\frac{\sum_{i=1}^{n}\left(X_i - \bar{X}\right)^2}{n-1}}$$

Where:

X_i = a result in the method reporting units obtained from analysis of a sample aliquot, i=1 to 3

$\bar{X}$ = mean of the three results, and

n = number of sample aliquots (3 in this case)

4.4.3.3 Calculate a preliminary MDL as follows:

Preliminary MDL = 6.96s

Where:

6.96 = Student's *t*-value appropriate for a 99% confidence level and two degrees of freedom

s = standard deviation of the results of analyses of the three replicates from section 4.4.3.2

4.4.3.4 If the preliminary MDL is in the range of 0.2—1.0 times the concentration in the spiked sample (section 4.3), analyze a minimum of four additional aliquots and proceed using the procedure in section 4.5. Use all seven measurements for calculation of the MDL. Otherwise, produce a new bulk sample per section 4.3, with the analyte at the concentration of the preliminary MDL and either repeat section 4.4.3, or proceed to section 4.5 for determination of the MDL.

4.5 MDL determination

4.5.1 Process at least seven aliquots of the test sample prepared in section 4.4 or section 4.4.3 through the entire analytical method.

4.5.2 Make all computations as specified in the method, with final results in the method-specified reporting units.

4.5.3 To obtain a valid MDL, all of the analytical results must be positive numbers. If any of the results are negative or zero, increase the test concentration (per section 4.3) and repeat the MDL procedure.

4.5.4 If more than seven aliquots are prepared and analyzed, the results from all the aliquots must be used to calculate the MDL, except as described in section 4.9.

4.6 Calculate the standard deviation, s, as follows:

$$s = \sqrt{\frac{\sum_{i=1}^{n}\left(X_i - \bar{X}\right)^2}{n-1}}$$

Where:

X_i = a result, in the method reporting units, obtained from analysis of a sample aliquot, i=1 to n

$\bar{X}$ = mean of the results, and

n = number of sample aliquots

Note to Section 4.6: When using a program such as a spreadsheet to calculate the standard deviation (s), make certain that the sample standard deviation, which uses (n − 1) in the denominator, is calculated, rather than the population standard deviation (σ), which uses n in the denominator.

4.7 Calculate the MDL

The MDL is calculated as:

$$MDL = s \times t_{(n-1,\ 1-\alpha=0.99)}$$

Where:

s = standard deviation of the results calculated in section 4.6

$t_{(n-1,\ 1-\alpha=0.99)}$ = Students' $_{t\text{-value}}$ appropriate for a 99% confidence level and (n − 1) degrees of freedom, from the table below.

TABLE OF STUDENT'S *t*-VALUES AT THE 99% CONFIDENCE LEVEL

Number of replicates for		Degrees of freedom (df)	$t_{(n-1,\ 1-\alpha=0.99)}$
Singles MDL (df = n − 1)	Iterative MDL (df = n − 2)		
7	N/A	6	3.143
8	N/A	7	2.998
9	N/A	8	2.896
10	N/A	9	2.821
11	N/A	10	2.764
12	N/A	11	2.718
13	14	12	2.681
14	15	13	2.650
15	16	14	2.624
16	17	15	2.602
17	18	16	2.583
18	19	17	2.567
19	20	18	2.552

Note to Section 4.7: Degrees of freedom = (n − 1) if a single MDL study is performed. If an iterative MDL study is performed, degrees of freedom = (n_h + n_l − 2), as described in section 4.8; N/A indicates that the number of degrees of freedom in this row does not apply to an iterative MDL study.

4.8 Iterate and verify the reasonableness of the MDL

When developing an MDL for a new or revised method, or when developing a matrix-specific MDL, the MDL procedure must be iterated and the reasonableness of the MDL determined using an F-test, as described in sections 4.8.1 through 4.8.4. When verifying a method-, matrix-, program-, or study-specific MDL, the MDL is determined as described in section 4.8.5 and iteration may not be necessary.

4.8.1 Iteration

When developing an MDL for a new or revised method, the spiking, analysis, and calculation steps (sections 4.3 to 4.6) must be repeated using a spike at no more than five times the MDL determined initially or in the most recent iteration, to confirm the reasonableness of the MDL.

4.8.2 Once the iteration is complete (*i.e.*, two successive MDL estimates have been produced), calculate the F-ratio (F) as:

$$F = \frac{\left(\frac{s_h^2}{n_h - 1}\right)}{\left(\frac{s_l^2}{n_l - 1}\right)}$$

Where:

s_h^2 = variance estimate from the higher spike concentration

s_l^2 = variance estimate from the lower spike concentration

n_h = number of observations at the higher concentration

n_l = number of observations at the lower concentration

4.8.3 For seven replicates at each concentration, the 90th percentile of the distribution of the F-statistic is 3.055.

4.8.3.1 If seven replicates were analyzed at each spike concentration and F >3.055, the two variances are different and the MDL determined at the higher spike concentration is not a reasonable estimate. In this case, return to section 4.3 and produce another sample at a test concentration below the higher of the two previous iterations, analyze a minimum of seven aliquots, calculate the MDL, and repeat the F-test in section 4.8.2.

4.8.3.2 If F ≤ 3.055 for seven replicates at each concentration, the two variances are not different. Proceed to section 4.8.4.

Note to Section 4.8.3.2: If more than seven replicates are used, the appropriate F-statistic is determined from the table below.

TABLE OF F-STATISTIC VALUES

	F-statistic			
	6	7	8	9
6	3.055	3.014	2.983	2.958
7	2.827	2.785	2.752	2.725
8	2.668	2.624	2.589	2.561
9	2.551	2.505	2.469	2.440

4.8.4 When the process has been iterated and the results pass the F-test in section 4.8.3, the final MDL is calculated by pooling the results from the two iterations that passed the F-test. The pooled standard deviation is calculated as:

$$s_{pooled} = \sqrt{\frac{(n_h - 1)(s_h)^2 + (n_l - 1)(s_l)^2}{(n_h + n_l - 2)}}$$

Where:

$(s_h)^2$ = variance estimate from the higher spike concentration

$(s_l)^2$ = variance estimate from the lower spike concentration

n_h = number of sample aliquots used for the higher spike concentration

n_l = number of sample aliquots used for the lower spike concentration

4.8.5 The pooled MDL is calculated using the pooled standard deviation and the Student's *t*-value for $(n_h + n_l - 2)$ degrees of freedom (*e.g.*, 12 degrees of freedom for two iterations with seven aliquots each).

$$MDL_{pooled} = s_{pooled} \times t_{(n_h + n_l - 2,\ 1-\alpha = 0.99)}$$

Where:

S_{pooled} = pooled standard deviation of the results

$t_{(nh\ +\ n1\text{-}2,\ 1\text{-}\alpha\ =\ 0.99)}$ = Student's *t*-value appropriate for a 99% confidence level and (n_h+n_l) aliquots

For 12 degrees of freedom, the t-value is 2.681. If more than seven replicates were used for either iteration, the appropriate *t*-value must be determined from the table given in section 4.7.

4.8.5 When verifying a method-, matrix-, program-, or study-specific MDL, the determined MDL is compared to the method-specified MDL, the MDL required to support a regulatory objective, or the MDL required to support an objective of a specific study or program. If the required MDL is not met for the analyte, make sure that all instrumentation and technical aspects of the process (reagent concentrations, temperature, clean glassware, proper dilutions, etc.) are checked and assessed to be working properly before a repeat of the analyses. If the second attempt fails, iteration at a more appropriate spiking level for that analyte is necessary until the requirement is met. If the regulatory, study, or program objective is not known, the MDL is verified if the determined MDL is less than or equal to the method-specified MDL.

4.9 Suspected Outliers

4.9.1 Results associated with a known, spurious error that occurred during analysis should be discarded, or where appropriate, corrected. Spurious errors include those that arise through human error or instrument malfunction, such as transposing digits in a number while recording data, arithmetical errors when calculating results, double-spiking of an aliquot, or the presence of an air bubble lodged in a spectrophotometer flow-through cell. Recording or arithmetical errors can and should be corrected, and the corrective actions documented prior to use of results. Results associated with spurious errors that cannot be corrected will invalidate the measurement and should not be incorporated into the MDL determination.

4.9.2 If random or spurious errors are suspected, it may be appropriate to apply a statistically accepted analysis of outliers, such as Grubbs test described below. Any outlying result should be considered with care to identify potential causes. It is generally not an accepted practice to reject a value purely on statistical grounds. Therefore, EPA recommends that when the cause of a potential outlier cannot be attributed to spurious causes, the MDL test be repeated for the analyte(s) in which such an outlier occurs.

Note to Section 4.9.2: If more than seven aliquots are prepared and analyzed, results from all aliquots must be used in the MDL determination unless they have been determined to be outliers as described above. Given the small number of replicates typically used to determine the MDL, it is inappropriate to use a data set that contains more than one statistical outlier.

4.9.3 The use of Grubbs test for outliers is described below, followed by an example (section 4.9.4).

4.9.3.1 Rank the n observed data points in the order of increasing numerical value: $X_1 \leq X_2 \leq ... \leq X_n$

4.9.3.2 Using the mean, $\bar{X}$, and standard deviation, s, from section 4.6, calculate:

$$T_l = \frac{(\bar{X} - X_1)}{s} \text{ and } T_n = \frac{(X_n - \bar{X})}{s}$$

Where:

X_1 = lowest observed value of X

X_n = highest observed value of X

4.9.3.3 Choose the larger of T_1 and T_n.

4.9.3.4 Compare the larger calculated value of T (*e.g.*, T_1 or T_n) with the critical value appropriate for the number of observations (n) from the table below. If T is larger than the critical value in the table, then the smallest (when testing T_1) or largest (when testing T_n) observed data point is considered to be an outlier with 95% confidence.

TABLE OF CRITICAL VALUES FOR T IN THE GRUBBS TEST

Number of data points (n)	Critical values for T
7	2.020
8	2.126
9	2.215
10	2.290
11	2.355
12	2.412
13	2.462
14	2.507
15	2.549

4.9.4 Example application of the outlier test

4.9.4.1 Consider the following ranked data set with seven observations: 0.0449, 0.0458, 0.0462, 0.0469, 0.0471, 0.0475, and 0.0508.

4.9.4.2 Its mean, $\bar{X}$, is 0.0470, and its standard deviation, s, is 0.0019.

4.9.4.3 Calculate: $T_1 = (0.0470 - 0.0449)/0.0019 = 1.132$ and $T_n = (0.0508 - 0.0470)/0.0019 = 2.007$

4.9.4.4 Select the larger value: $T = \max\{1.132, 2.007\} = 2.007$

4.9.4.5 Compare T with the corresponding critical value in the second line of the table above, where n=7 and the critical value of T = 2.020.

Since the calculated value of T, 2.007, is not larger than the critical value in the table, 2.020, there is insufficient evidence to conclude that any of the observed data points is an outlier, and the MDL would be calculated from all seven results.

5.0 References

5.1 Currie, Lloyd A. (1968), Limits for Quantitative Detection and Quantitative Determination, Analytical Chemistry 40: 586–593.

5.2 Currie, Lloyd A. (1995), Nomenclature in Evaluation of Analytical Methods including Detection and Quantification Capabilities, Pure and Appl. Chem. 67:10, 1699–1722.

5.3 Glaser, J.A., D.L. Foerst, J.D. McKee, S.A. Quave and W.L. Budde (1981), Trace Analyses for Wastewaters, Environ. Sci. Technol., 15:1426.

5.4 Keith, Lawrence H., *et al.* (1983), Principles of Environmental Analysis, Analytical Chemistry 55:14, 2210–2218.

5.5 McDougal, Daniel, *et al.* (1980), Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry, Analytical Chemistry 52:14, 2242–2249.

B. Definition and Procedure for the Determination of the Minimum Level of Quantitation (ML)

1.0 Definition

The minimum level of quantitation (ML) is the lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point for the analyte. The ML represents the lowest concentration at which an analyte can be measured with a known level of confidence. It may be equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. It is functionally analogous to the ''determination limit'' described by Currie (1968) and the Limit of Quantification (LOQ) described by the American Chemical Society (Keith *et al.*,1980, McDougal *et al.*, 1983) and Currie (1995).

Note to Section 1.0: The ML is directed at obtaining a 10% relative standard deviation for determination of an analyte in an environmental sample. This error may be reduced by making multiple determinations of the analyte in the sample.

2.0 Scope and Application

2.1 The ML is typically established by the organization that develops or modifies an analytical test method. A laboratory that employs the method would be expected to include calibration standards that encompass the ML when it calibrates an analytical system, unless a higher quantitation level is acceptable for a specific application. If an ML is not specified in a method, a laboratory may use the ML procedure to establish the lowest calibration point.

2.2 This procedure is intended for use in EPA's Clean Water Act (CWA) programs. An alternative procedure may be used (*e.g.*, from a voluntary consensus standards body) to establish the sensitivity of an analytical method provided the resulting quantitation limit meets the sensitivity needs (*i.e.*, data quality objective) for the specific application.

2.3 Laboratories are encouraged, but not required, to periodically demonstrate recovery of the target analyte near the published ML or laboratory-established ML by preparing a reference matrix sample spiked at the ML and analyzing it using all sample handling and processing steps described in the method. If the method does not provide acceptance criteria for such an ML standard, the laboratory can make an assessment of whether acceptance criteria for other spiked reference matrix samples (*e.g.*, laboratory control samples, laboratory fortified blanks, ongoing precision and recovery samples, etc.) are appropriate to evaluate analyte recovery at the ML. Alternatively, the laboratory may develop its own acceptance criteria based on data gathered by the laboratory over time.

3.0 Procedure

3.1 The ML is based on 10 times the standard deviation of the results of replicate analyses of a matrix containing the analyte. The method detection limit (MDL) is also based on the same standard deviation, multiplied by the Student's *t*-value appropriate for a 99% confidence level and corresponding degrees of freedom. Because the standard deviation may not be readily available, the ML is often calculated as a factor times the MDL.

3.1.1 Calculating the ML based on MDL study data

When available, obtain the actual standard deviation value from the MDL study and calculate the ML directly, as 10 times the standard deviation. If an iterative MDL study is performed, calculate the MDL as 10 times the pooled standard deviation.

3.1.2 Calculating the ML based on the MDL Assuming a single iteration of seven replicates is used to determine the MDL, the number of degrees of freedom is 6, and the Student's *t*-value is 3.143. Therefore, the MDL is:

$MDL = 3.143 \times s$

and the ML is:

$$ML = 10 \times s = \frac{10}{3.143} \times MDL \approx 3.18 \times MDL$$

3.1.3 If the MDL is calculated from other than seven replicates or using the iterative procedure, the factor of 3.18 will change, and the table below is used to establish the correct multiplier. For example, if an iterative MDL study is performed consisting of exactly 7 replicates in each iteration, the resulting pooled MDL would incorporate 12 degrees of freedom, and the equation for the ML above would be modified accordingly, using a multiplier of 3.73.

TABLE OF STUDENT'S *t*-VALUES AT THE 99% CONFIDENCE LEVEL AND ML MULTIPLIERS

Number of replicates for		Degrees of freedom (df)	$t_{(n-1,1-\alpha=0.99)}$	ML multiplier
Single MDL (df=n − 1)	Iterative MDL (df=n − 2)			
7	N/A	6	3.143	3.18
8	N/A	7	2.998	3.34
9	N/A	8	2.896	3.45
10	N/A	9	2.821	3.54
11	N/A	10	2.764	3.62
12	N/A	11	2.718	3.68
13	14	12	2.681	3.73
14	15	13	2.650	3.77
15	16	14	2.624	3.81
16	17	15	2.602	3.84
17	18	16	2.583	3.87
18	19	17	2.567	3.90
19	20	18	2.552	3.92

Note to Table: Degrees of freedom = (n − 1) if a single iteration MDL study is performed and (n_h + n_l − 2) if an iterative MDL study is performed; N/A indicates that the number of degrees of freedom in this row does not apply to an iterative MDL study.

4.0 Rounding

The ML may be used to establish the lowest calibration point for the analyte. Therefore, in order to facilitate the preparation of calibration standards containing the analyte without undue difficulty, the ML may be rounded to the nearest multiple of 1, 2, or 5×10^n, where n is an integer.

5.0 References

5.1 Currie, Lloyd A. (1968), Limits for Quantitative Detection and Quantitative Determination, Analytical Chemistry 40: 586–593.

5.2 Currie, Lloyd A. (1995), Nomenclature in Evaluation of Analytical Methods including Detection and Quantification Capabilities, Pure and Appl. Chem. 67:10, 1699–1722.

5.3 Glaser, J.A., D.L. Foerst, J.D. McKee, S.A. Quave and W.L. Budde (1981), Trace Analyses for Wastewaters, Environ. Sci. Technol., 15:1426.

5.4 Keith, Lawrence H., *et al.* (1983), Principles of Environmental Analysis, Analytical Chemistry 55:14, 2210–2218.

5.5 McDougal, Daniel, *et al.* (1980), Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry, Analytical Chemistry 52:14, 2242–2249.

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