Appendix A
Literature Search Regarding
Detection and Quantitation Limit Approaches

Introduction

Beginning in 2001, DynCorp conducted a search of published literature to identify articles that discuss detection and quantitation limit approaches. This literature search effort was conducted under EPA Contract No. 68-C-01-091 to support an evaluation of detection and quantitation limit approaches by the EPA's Office of Water.

The principal goal of this literature search was to determine if any new detection or quantitation limit approaches had been published since an earlier search conducted for EPA by Science Applications International Corporation (SAIC) in 1997 and 1998. That search resulted in an annotated bibliography developed by SAIC and delivered to EPA in 1998.

In August 2002, EPA included the literature search results in a draft Technical Support Document (TSD) that was submitted for formal peer review. As part of the charge to the peer reviewers, EPA asked them to identify any additional references. Following EPA's review of the suggested additional references, references relevant to the TSD were added.

How the search was conducted

This search was conducted using two major techniques:

- a search of an on-line citation index (an index of articles cited by other authors), and
- a general on-line search of literature.

On-line citation index search

Because the search was intended to identify detection and quantitation limit approaches and not specific numeric limits associated with a particular analytical method, DynCorp began by searching for references to the major approaches known to EPA. These included the Agency's method detection limit (MDL) and any other terms that have been suggested to the Agency as alternative detection or quantitation limit approaches. In addition to searching for these approaches, DynCorp also searched the citation index to identify references to the original authors of these approaches and for any other authors who either cited the original approaches, the original papers underlying those approaches, or the authors of those approaches. DynCorp used a similar approach to find any papers that cited the references identified in the earlier literature search by SAIC.

DynCorp staff evaluated the full title of each identified citation to determine its relevance to EPA's objective. Where available electronically and at no additional cost, DynCorp staff also reviewed the abstract and/or full paper to further characterize relevance. All papers that were determined to be relevant, or even possibly relevant, were obtained in hardcopy or electronic format for evaluation by EPA.

After reviewing all papers determined to be relevant to EPA's objective, DynCorp examined all of the references cited in those papers to identify additional papers of interest. These, too, were obtained in hardcopy or electronic format for evaluation by EPA, except where noted below.

General on-line literature search

DynCorp performed an on-line direct search of published literature (e.g., a literature database of published articles, not a citation index) using general terms such as "detection limit," "quantitation limit," or "calibration." As expected, this approach returned a very large numbers of papers that mention these terms, even if the focus of the paper was on something far removed from the development or assessment of approaches about detection and quantitation, and proved to be of limited value in serving EPA's objectives for the search. Therefore, DynCorp discontinued this effort and narrowed the on-line literature search to a search for additional, uncited works by authors of the approaches known to EPA or identified through the citation index approach.

Papers determined to be relevant to EPA's objective were obtained in electronic or hardcopy format for evaluation by EPA, except where noted below.

How the results are presented

DynCorp identified a total of 161 relevant publications using the approach described above. Thirty-three (33) of these publications were also identified in the earlier search by SAIC. Of the 128 remaining publications, 35 were published since the SAIC search was completed.

The peer reviewers suggested additional publications covering a variety of topics, including: quality control, analysis of mercury, and approaches to dealing with censored data. EPA reviewed the citations from the peer reviewers and determined that 20 directly addressed detection or quantitation approaches. In particular, EPA noted that the issue of censored data applies regardless of the specific detection or quantitation limit associated with the data, so those citations dealing with censored data were not included.

Each of the 181 publications identified in the search is listed in Attachment 1, which provides the title, year of publication, authors, and source citation. The citations for the 33 papers identified in the earlier search by SAIC are included in the attachment, and can be identified by the phrase "annotated only" in parentheses after the title of the paper.

The final column of the attached spreadsheet is labeled "Category." All of the citations identified in the SAIC literature search and the current search conducted by DynCorp were placed in one of the six following categories, based on the principal characteristic of the article:

- Background - The citation discusses background information (including early works by Currie, Kaiser, and others).
- Calibration concept - The citation primarily deals with calibration of analytical instrumentation
- Critique - The major thrust of the citation is to critique one or more approaches, as opposed to introducing a new approach
- Multi-laboratory approach - The citation describes an approach to developing detection and/or quantitation limits that relies on multi-laboratory measurements
- Single-laboratory approach - The citation describes an approach to developing detection and/or quantitation limits that relies on single-laboratory measurements
- Single-laboratory, multi-level approach - The citation describes an approach to developing detection and/or quantitation limits that relies on single-laboratory measurements but explicitly includes multiple concentrations.

Although there is some degree of overlap between categories, and some papers could probably be classified in more than one category, each citation was classified into only one category for the purposes of this search.

A seventh category called "Not found" was used for three papers that were identified in the literature search, but for which copies could not readily be obtained. One paper is from a German journal that was not available via interlibrary loan. A second article also was not available via interlibrary loan. The third citation is an abstract by Currie, from 1983. Given that the work of Currie is well-represented in the other citations and the fact that this citation appears to be only an abstract, additional efforts were not expended to obtain a copy.

The 20 publications suggested by the peer reviewers were all included at the end of the list, under an eighth category called "Suggested by a peer reviewer."

The references presented in the table were sorted by category and year of publication and are displayed with the most recent citations in each category first.

Summary

The principal goal of this literature search effort was to determine if any new detection or quantitation limit approaches had been published in the literature since the search by SAIC in 1997 - 1998. As anticipated, citations were identified that relate to the recent efforts of the International Organization for Standardization (ISO), the International Union of Pure and Applied Chemists (IUPAC), and the ASTM International. Additional articles critiquing various approaches were identified as well. However, no previously unknown detection or quantitation limit approaches were uncovered as a result of this effort. Likewise, the references suggested by the peer reviewers provided additional details and applications of existing detection and quantitation approaches, but did not suggest any approaches that had not already been identified.

Results of the 2001 Literature Search

Title	Year	Author	Source	Category
Some Case Studies of Skewed (and other ab"normal) Data Distributions Arising in Low-Level Environmental Research	2001	L.A. Currie	Fresenius Journal of Analytical Chemistry 370: 705-718	Background
Legislative Limits Below Detection Capability	2000	S.L.R. Ellison, V.J. Barwick, A. Williams	Accreditation Quality Assurance 5: 308-313	Background
International Recommendations Offered on Analytical Detection and Quantification Concepts and Nomenclature	1999	L.A. Currie	Analytica Chimica Acta 391: 103	Background
Detection and Quantitation Limits: Origins and Historical Overview	1999	L.A. Currie	Analytica Chimica Acta 391: 127-134	Background
1996 ASMS Fall Workshop: Limits to Confirmation, Quantitation, and Detection	1997	R. Baldwin, R.A. Bethem, R.K. Boyd, W.L. Budde, T. Cairns, R.D. Gibbons, J.D. Henion, M.A. Kaiser,	Journal of the American Society for Mass Spectrometry 8: 1180-1190	Background
Measurement precision and 1/f Noise in Analytical Instruments	1996	Y. Hayashi, R. Matsuda, R.B. Poe	Journal of Chromatography A 722: 157-167	Background
Fossil- and Bio-mass Combustion: C-14 for Source Identification, Chemical Tracer Development, and Model Validation	1994	L.A. Currie, G.A. Klouda, D.B. Klinedinst, A.E. Sheffield, A.J.T. Jull, D.J. Donahue, M.V. Connolly	Nuclear Instr. And Methods in Physics Res. B 92: 404-409	Background
Interlaboratory Comparison of Instruments Used for the Determination of Elements in Acid Digestates of Solids	1994	D.E. Kimbrough, J. Wakakuwa	Analyst 119: 383-388	Background
Throwaway Data	1994	L.H. Keith	Environmental Science & Technology 28: 389A-390A	Background
EPA's Office of Water Surges Toward MDL Solution	1994	Larry Keith	Radian	Background
In Pursuit of Accuracy: Nomenclature, Assumptions, and Standards	1992	L.A. Currie	Pure & Applied Chemistry 64:455-472	Background
Interlaboratory Aspects of Detection Limits Used for Regulatory and Control Purposes	1988	L.B. Rogers	ACS Symposium Series 361:94-108	Background
Noise and Detection Limits in Signal-Integrating Analytical Methods	1988	H.C. Smit, H. Steigstra	ACS Symposium Series 361:126-148	Background
Effects of Analytical Calibration Models on Detection Limit Estimates	1988	K.G. Owens, C.F. Bauer, C.L. Grantr	ACS Symposium Series 361:194-207	Background
Real-World Limitations to Detection	1988	D. Kurtz, J. Taylor, L. Sturdivan, W. Crummett, C. Midkiff, R. Watters Jr, L. Wood, W. Hanneman, W. Horwitz	ACS Symposium Series 361:288-316	Background
Detection Limits - A Systematic Approach to Detection Limits is Needed When Trace Determinations are to be Performed	1986	S.A. Borman	Analytical Chemistry 58: A986	Background
Chemometrics and Analytical Chemistry	1984	L.A. Currie	Chemometrics 56: 115-146	Background
Quality Control in Water Analyses	1983	C. Kirchmer	ES&T 17: 174A-181A	Background
Validation of Analytical Methods	1983	J.K. Taylor	Analytical Chemistry 55: 600A-602A, 608A	Background

Title	Year	Author	Source	Category
Trace Analyses for Wastewaters - Author's response	1982	D. Foerst	Envir. Sci. & Tech. 16: 430A - 431A	Background
Zur Theorie der Eichfunktion bei der spektrochemischen Analyse	1982	V.H. Kaiser	DK 535: 309-319	Background
The Reliability of Detection Limits in Analytical Chemistry	1980	J.D. Winefordner, J.L. Ward	Analytical Letters 13: 1293-1297	Background
A Review and Tutorial Discussion of Noise and Signal-to-Noise Ratios in Analytical Spectrometry - I. Fundamental Principles of Signal-to-Noise Ratios	1978	C.T.J. Alkemade, W. Snelleman, G.D. Boutilier, B.D. Pollard, J.D. Winefordner, T.L. Chester, N. Omenetto	Spectrochimica Acta 33B: 383-399	Background
A Review and Tutorial Discussion of Noise and Sign-to-Noise Ratios in Analytical Spectrometry - II. Fundamental Principles of Signal-to-Noise Ratios	1978	G.D. Boutilier, B.D. Pollard, J.D. Winefordner, T.L. Chester, N. Omenetto	Spectrochimica Acta 33B: 401-415	Background
A Tutorial Review of Some Elementary Concepts in the Statistical Evaluation of Trace Element Measurements	1978	P.W.J.M. Boumans	Spectrochimica Acta 33B: 625-634	Background
Analysis of Lead in Polluted Coastal Seawater	1976	C. Patterson, D. Settle, B. Glover	Marine Chemistry 4: 305-319	Background
Multielement Analysis with an Inductively Coupled Plasma/Optical Emission System	1976	R.M. Ajhar, P.D. Dalager, A.L. Davison	American Laboratory 72-78	Background
Interlaboratory Lead Analyses of Standardized Samples of Seawater	1974	P. Brewer, N. Frew, N. Cutshall, J.J. Wagner, R.A. Duce, P.R. Walsh, G.L. Hoffman, J.W.R. Dutton, W.F. Fitzgerald	Marine Chemistry 2: 69-84	Background
Statistical and Mathematical Methods in Analytical Chemistry	1972	L.A. Currie, J.J. Filliben, J.R. DeVoe	Anal. Chem. 44: 497R-512R	Background
Studies of Flame and Plasma Torch Emission for Simultaneous Multi-Element Analysis- I. Preliminary Investigations	1972	P.W.J.M. Boumans, F.J. De Boer	Spectrochimica Acta 27B: 391-414	Background
Quantitative Determination: Application to Radiochemistry	1968	Lloyd Currie	Anal. Chem. 40: 586-593	Background
Qualitative and Quantitative Sensitivity in Flame Photometry	1966	J. Ramirez-Munoz	Talanta 13: 87-101	Background
The Limit of Detection of Analytical Methods	1962	J.B. Roos	Analyst 87: 832-833	Background
A Careful Consideration of the Calibration Concept	2001	S.D. Phillips, W.T. Estler, T. Doiron, K.R. Eberhardt, M.S. Levenson	Journal of Research of the National Institute of Standards and Technology 106: 371-379	Calibration
Weighted Random-Effects Regression Models with Application to Interlaboratory Calibration	2001	R.D. Gibbons, D.K. Bhaumik	Technometrics 43: 192-198	Calibration
Guidelines for Calibration in Analytical Chemistry-Part I. Fundamentals and Single Component Calibration (IUPAC recommendations 1998)	1998	K. Danzer, L.A. Currie	Pure and Applied Chemistry 70: 993-1014	Calibration
A Comparison of Uncertainty Criteria for Calibration	1996	R.W. Mee, K.R. Eberhardt	Technometrics 38: 221-229	Calibration
Constant-Width Calibration Intervals for Linear Regression	1994	K.R. Eberhardt, R.W. Mee	Journal of Quality Technology 26: 21-29	Calibration
Regression and Calibration with Nonconstant Error Variance	1990	M. Davidian, P.D. Haaland	Chemometrics and Intelligent Laboratory Systems 9: 231-248	Calibration

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Calibration with Randomly Changing Standard Curves	1989	D.F. Vecchia, H.K. Iyer, P.L. Chapman	Technometrics 31: 83-90	Calibration
Linear Calibration When the Coefficient of Variation is Constant	1988	Y.C. Yao, D.F. Vecchia, H.K. Iyer	Probability and Statistics: Essays in Honor of Franklin A. Graybill, 297-309	Calibration
Analytical Method Comparisons by Estimates of Precision and Lower Detection Limit	1986	D.M. Holland, F.F. McElroy	Environmental Science & Technology 20: 1157-1161	Calibration
Design Considerations for Calibration	1986	J.P. Buonaccorsi	Technometrics 28: 149-155	Calibration
Multivariate Calibration when the Error Covariance Matrix is Structured	1985	T. Naes	Technometrics 27: 301-311	Calibration
An Implementation of the Scheffé Approach to Calibration Using Spline Functions, Illustrated by a Pressure-Volume Calibration	1982	J.A. Lechner, C.P. Reeve, C.H. Spiegelman	Technometrics 24: 229-234	Calibration
Measuring and Maximizing Precision in Analyses Based on Use of Calibration Graphs	1982	D.G. Mitchell, J.S. Garden	Talanta 29: 921-929	Calibration
Calibration in Quantitative Analysis: Part2. Confidence Regions for the Sample Content in the Case of Linear Calibration Relations	1981	J. Agterdenbos, F.J.M.J. Maessen, J. Balke	Analytica Chimica Acta 132: 127-137	Calibration
Design Aspects of Scheffe's Calibration Theory using Linear Splines	1980	C.H. Spiegelman, W.J. Studden	Journal of Research of the National Bureau of Standards 85: 295-304	Calibration
Nonconstant Variance Regression Techniques for Calibration-Curve-Based Analysis	1980	J.S. Garden, D.G. Mitchell, W.N. Mills	Anal. Chem. 52: 2310-2315	Calibration
Calibration in Quantitative Analysis	1979	J. Agterdenbos	Analytica Chimica Acta 108: 315-323	Calibration
Calibration Curves with Nonuniform Variance	1979	L. Schwartz	Analytical Chem. 51: 723-727	Calibration
Elimination of the Bias in the Course of Calibration	1978	L.J. Naszódi	Technometrics 20: 201-205	Calibration
Optimal Designs for the Inverse Regression Method of Calibration	1973	M.A. Thomas, R.H. Myers	Communications in Statistics 2: 419-433	Calibration
A Statistical Theory of Calibration	1973	H. Scheffé	The Annals of Statistics 1: 1-37	Calibration
On the Problem of Calibration	1972	G.K. Shukla	Technometrics 14: 547-553	Calibration
Statistical Processing of Calibration Data in Quantitative Analysis by Gas Chromatography	1970	P. Bocek, J. Novak	J. Chromatog. 51: 375-383	Calibration
Estimation of a Linear Function for a Calibration Line: Consideration of a Recent Proposal	1969	J. Berkson	Technometrics 11: 649-660	Calibration
A Note on Regression Methods in Calibration	1969	E.J. Williams	Technometrics 11: 189-192	Calibration
Classical and Inverse Regression Methods of Calibration in Extrapolation	1969	R.G. Krutchkoff	Technometrics 11: 605-608	Calibration
Optimal Experimental Designs for Estimating the Independent Variable in Regression	1968	R.L. Ott, R.H. Myers	Technometrics 10: 811-823	Calibration

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Classical and Inverse Regression Methods of Calibration	1967	R.G. Krutchkoff	Technometrics 9: 425-439	Calibration
The Interpretation of Certain Regression Methods and their Use in Biological and Industrial Research	1939	C. Eisenhart	The Annals of Mathematical Statistics 10: 162-186	Calibration
The Three "Rs" for Relevant Detection, Reliable Quantitation and Respectable Reporting Limits	2000	Ann Rosecrance	Env. Testing & Anal. 9: 13,50	Critique
Detection and Quantification Capabilities and the Evaluation of Low-Level Data: Some International Perspectives and Continuing Challenges	2000	L.A. Currie	Journal of Radioanalytical and Nuclear Chemistry 245: 145-156	Critique
Realistic Detection Limits from Confidence Bands	1999	J.R. Burdge, D.L. McTaggart, S.O. Farwell	Journal of Chemical Education 76: 434-439	Critique
Response to Comment on "An Alternative Minimum Level Definition for Analytical Quantification"	1999	Henry Kahn, William Telliard, Chuck White	Env. Sci. & Tech. 33: 1315	Critique
Comment on "An Alternative Minimum Level Definition for Analytical Quantification"	1999	H.G. Rigo	Env. Sci & Tech. 33: 1311-1312	Critique
Response to Comment on "An Alternative Minimum Level Definition for Analytical Quantification"	1999	Robert Gibbons, David Coleman, Ray Maddalone	Env. Sci. & Tech. 33: 1313-1314	Critique
Comment on "An Alternative Minimum Level Definition for Analytical Quantification"	1998	Henry Kahn, William Telliard, Chuck White	Envir. Sci & Tech 32: 2346-2348	Critique
Response to Comment on "An Alternative Minimum Level Definition for Analytical Quantification"	1998	Robert Gibbons, David Coleman, Ray Maddalone	Envir. Sci & Tech 32: 2349-2353	Critique
A Discussion of Issues Raised by Lloyd Currie and a Cross Disciplinary View of Detection Limits and Estimating Parameters that are Often At or Near Zero	1997	C.H. Spiegelman	Chemometrics and Intelligent Laboratory Systems 37: 183-188	Critique
A Mock Trial for Critical Values (Detection Limits)	1997	C.H. Spiegelman, P. Tarlow	STATS: The Magazine for Students of Statistics 20: 13-16	Critique
Comment on "An Alternative Minimum Level Definition for Analytical Quantification"	1997	David Kimbrough	Envir. Sci. & Tech. 31: 3727-3728	Critique
The Smallest Concentration	1997	R.F. Moran, E.N. Brown	Clinical Chemistry 43: 856-857	Critique
A Statistical Overview of Standard (IUPAC and ACS) and New Procedures for Determining the Limits of Detection and Quantification: Application to Voltammetric and Stripping Techniques (Technical Report)	1997	J. Mocak, A.M. Bond, S. Mitchell, G. Scollary	Pure and Applied Chemistry 69: 297-328	Critique
Response to Comment on "An Alternative Minimum Level Definition for Analytical Quantification"	1997	R.D. Gibbons, D.E. Coleman, R.F. Maddalone	Envir. Sci. & Tech 31: 3729-3731	Critique
Some Conceptual and Statistical Issues in Analysis of Groundwater Monitoring Data	1996	R.D. Gibbons	Environmetrics 7: 185-199	Critique
Some Statistical and Conceptual Issues in the Detection of Low Level Environmental Pollutants	1995	Robert Gibbons	Environ. & Ecol. Statistics 2: 125-167	Critique

Title	Year	Author	Source	Category
Comment on "Method Detection Limits in Solid Waste Analysis"	1995	D.E. Coleman	Environmental Science & Technology 29: 279-280	Critique
Comment on "Method Detection Limits in Solid Waste Analysis"	1995	Janice Wakakuwa, David Kimbrough	Envir. Sci. & Tech. 29: 281-282	Critique
"You Can't Compute With Less-Thans"	1994	Ken Osborn, Ann Rosecrance	East Bay Municipal Utility District, Core Laboratories	Critique
Limits of Detection	1994	N. Cressie	Chemometrics Intelligent Laboratory Systems 22: 161-163	Critique
Conflicting Perspectives About Detection Limits and About the Censoring of Environmental Data	1994	M.J.R. Clark, P.H. Whitfield	Water Resources Bulletin 30: 1063-1079	Critique
Limit of Discrimination, Limit of Detection and Sensitivity in Analytical Systems	1994	R. Ferrus, M.R. Egea	Analytica Chimica Acta 287: 119-145	Critique
Discussion of: A Study of the Precision of Lead Measurements at Concentrations Near the Method Limit of Detection	1994	B.R. Nott, R.R. Maddalone	Water Environment Research 66: 853-854	Critique
Limits of Detection Methodologies	1993	J. Lindstedt	Plating and Surface Finishing 80: 81-86	Critique
Method Detection Limits in Solid Waste Analysis	1993	David Kimbrough, Janice Wakakuwa	Enviro. Sci. & Tech 27: 2692-2699	Critique
Defining the Limits	1993	G. Stanko, W. Krochta, A. Stanley, T. Dawson, K. Hillig, R. Javick, R. Obryckl, B. Hughes, F. Saksa	Environmental Lab 1: 16-20	Critique
A Study of the Precision of Lead Measurements at Concentrations Near the Method Limit of Detection	1993	P.M. Berthouex	Water Environment Research 65: 620-629	Critique
Detection Limit Concepts: Foundations, Myths, and Utilization	1992	D.A. Chambers, S.S. Dubose, E.L. Sensintaffar	Health Phys. 63: 338-340	Critique
Difficulties Related to Using Extreme Percentiles for Water Quality Regulations	1991	P. M. Berthouex, Ian Hau	Research Journal WPCF 63: 873-879	Critique
A Simple Rule for Judging Compliance Using highly Censored Samples	1991	P. M. Berthouex, Ian Hau	Research Journal WPCF 63: 880-886	Critique
Current Method for Setting Dioxin Limits in Water Requires Reexamination	1990	J. LaKind, E. Rifkin	Env. Sci. & Tech 24: 963-965	Critique
Kaiser 3-Sigma Criterion - A Review of the Limit of Detection	1990	L.S. Oresic, V. Grdinic	Acta Pharmaceutica Jugoslavica 40: 21-61	Critique
MCL Noncompliance: Is the Laboratory at Fault?	1990	Steven Koorse	AWWA p53-58	Critique
Qualitative or Quantitative Characterization of Spectrographic Methods? The Detection and Determination Limits	1990	Karol Florian	Chemia Analityczna 35:129-139	Critique
False Positives, Detection Limits, and Other Laboratory Imperfections: The Regulatory Implications	1989	Steven Koorse	Environmental Law Reporter 19: 10211-10222	Critique
Evaluation of Detection Limit Estimators	1988	F.C. Garner, G.L. Robertson	Chemometrics and Intelligent Laboratory Systems 3: 53-59	Critique
Chemometrics - Measurement Reliability	1988	K. Castaneda-Mendez	Clinical Chemistry 34: 2494-2498	Critique
The Detection Limit	1988	P.S. Porter, R.C. Ward, H.F. Bell	Environmental Science & Technology 22: 856-861	Critique

Title	Year	Author	Source	Category
Estimation of Detection Limits for Environmental Analytical Procedures - A Tutorial	1988	Cliff Kirchmer	ACS Symposium Series 361: 78-93	Critique
Limits of Detection	1984	J.K. Taylor	Analytical Chemistry 56: 130A	Critique
Clarification of the Limit of Detection in Chromatography	1984	J.P. Foley, J.G. Dorsey	Chromatographia 18: 503-511	Critique
Limit of Detection: A Closer Look at the IUPAC Definition	1983	Gary Long, J.D. Winefordner	Analytical Chem. 55: 712-724	Critique
Trace Analyses for Wastewaters	1982	C.J. Kirchmer	Envir. Sci. & Tech. 16: 430A	Critique
A comparison of statistical and empirical detection limits	1998	G.C.C. Su	Journal of AOAC International 81: 105-110	Multilab
Challenges in Regulatory Environmetrics	1997	C.B. Davis	Chemometrics Intelligent Laboratory Systems 37: 43-53	Multilab
Determining Quantitation Levels for Regulatory Purposes	1996	P.F. Sanders, R.L. Lippincott, A. Eaton	Journal American Water Works Association 88: 104-114	Multilab
Defining Detection and Quantitation Levels	1993	Raymond Maddalone, James Rice, Ben Edmondson, Babu Nott, Judith Scott	Water Envir. & Tech. Jan.93: 41-44	Multilab
Concept 2000-A Statistical Approach for Analytical Practice - Part I: Limits of Detection, Identification, and Determination	1999	Hadrich J et al.	Deutsche Lebensmittel-Rundschau 1999, 95(10), 428-436	not found
Statistics and Environmental Policy: Case Studies from Long-Term Environmental Monitoring Data	1999	Goudey R et al.	Novart FDN Sym 220; 144-157	not found
The Many Dimensions of Detection in Chemical Analysis	1983	Currie LA	Abstracts of Papers of the American Chemical Society, 185 (Mar), 63-PEST	not found
A Practical Strategy for Determining and Verifying Detection Limits	2001	T. Georgian, K.E. Osborn	Env. Testing & Analysis 10: 13-14	Single lab
Review of the Methods of the US Environmental Protection Agency for Bromate Determination and Validation of Method 317.0 for Disinfection By-Product Anions and Low -Level Bromate	2001	D.P. Hautman, D.J. Munch, C. Frebis, H.P. Wagner, B.V. Pepich	Journal of Chromatography A 920: 221-229	Single lab
Comparison of Detection Limits in Environmental Analysis - Is it Possible? An Approach on Quality Assurance in the Lower Working Range by Verification	2001	S. Gelb, J.W. Einax	Fresenius Journal of Analytical Chemistry 370: 673-678	Single lab
On the Assessment of Compliance with Legal Limits, Part I: Signal and Concentration Domains	2001	E. Desimoni, S. Mannino, B. Brunetti	Accreditation Quality Assurance 6: 452-458	Single lab
Capability of Detection - Part 2	2000	ISO	ISO 11843-2	Single lab
Nomenclature in Evaluation of Analytical Methods Including Detection and Quantitation Capabilities (IUPAC Recommendations 1995)	1999	L.A. Currie	Analytica Chimica Acta 391: 105-126	Single lab
New Reporting Procedures Based on Long-Term Method Detection Limits and Some Considerations for Interpretations of Water-Quality Data Provided by the U.S. Geological Survey National Water Quality Laboratory	1999	C. J. Oblinger Childress, W. T. Foreman, B. F. Connor, and T. J. Maloney	USGS Open-File Report 99-193, 19 pages.	Single lab

Title	Year	Author	Source	Category
Analyses of Polychlorinated Biphenyls and Chlorinated Pesticides in Biota: Method and Quality Assurance	1999	P. Cleemann, G.B. Paulsen	Journal of AOAC International 82: 1175-1184	Single lab
Detection Limits of Organic Contaminants in Drinking Water	1998	W.M. Draper, J.S. Dhoot, J.S. Dhaliwal, J.W. Remoy, S.K. Perera, F.J. Baumann	Journal of the American Water Works Association 90: 82-90	Single lab
Detection: International Update, and Some Emerging Di-lemmas Involving Calibration, the Blank, and Multiple Detection Decisions	1997	L.A. Currie	Chemometrics and Intelligent Laboratory Systems 37: 151-181	Single lab
Regulations - From an Industry Perspective or Relationships Between Detection Limits, Quantitation Limits, and Significant Digits	1997	D. Coleman, J. Auses, N. Grams	Chemometrics and Intelligent Laboratory Systems 37: 71-80	Single lab
Capability of Detection - Part 1	1997	ISO	ISO 11843-1	Single lab
Determination of Site-Specific Effluent Detection Limits	1996	George Neserke, Harold Taylor	Water Env. Res. 66: 115-119	Single lab
Multivariate Detection Limits Estimators	1996	R. Boque, F.X. Rius	Chemometrics and Intelligent Laboratory Systems 32: 11-23	Single lab
Nomenclature in Evaluation of Analytical Methods including Detection and Quantification Capabilities	1995	Lloyd Currie	Pure & Appl. Chem. 67: 1699-1723	Single lab
Reporting Low-Level Analytical Data Third Draft (1995-11-08) -- New Project of Commission V.I., International Union of Pure and Applied Chemistry	1995	William Horwitz	IUPAC	Single lab
IUPAC Recommendations for Defining and Measuring Detection and Quantification Limits	1994	LA Currie, W. Horwitz	Analuses Magazine 22: 24-26	Single lab
Recommendations for the Presentation of Results of Chemical Analysis	1994	L.A. Currie, G. Svehla	Pure & Applied Chemistry 66: 595-608	Single lab
Detarchi-A Program for Detection Limits with Specified Assurance Probabilities and Characteristic Curves of Detection	1994	L. Sarabia, M.C. Ortiz	TRAC-Trends in Analytical Chemistry 13: 1-6	Single lab
Quality Control Level: An Alternative to Detection Levels	1994	D.E. Kimbrough, J. Wakakuwa	Environmental Science & Technology 28: 338-345	Single lab
Multivariate Decision and Detection Limits	1993	A. Singh	Analytica Chimica Acta 277: 205-214	Single lab
A Model of Measurement Precision at Low Concentrations	1993	P.M. Berthouex, D.R. Gan	Water Environment Research 65: 759-763	Single lab
Robust Procedure for Calibration and Calculation of the Detection Limit of Trimipramine by Adsorptive Stripping Voltametry at a Carbon Paste Electrode	1993	M.C. Ortiz, J. Arcos, J.V. Jurarros, J. Lopez-Palacios, L.A. Sarabia	Analytical Chemistry 65: 678-682	Single lab
Nondetects, Detection Limits, and the Probability of Detection	1991	D. Lambert, B. Peterson, I. Terpenning	JASA 86: 266-277	Single lab
Detection Limits: For Linear Calibration Curves with Increasing Variance and Multiple Future Detection Decisions	1991	R.D. Gibbons, F.H. Jarke, K.P. Stoub	Waste Testing and Quality Assurance: ASTM STP 1075, D. Friedman, Ed., American Society for Testing and Materials, Philadelphia 3: 337-390	Single lab
Limits of Detection in Multivariate Calibration	1991	G. Bauer, W. Wegscheider, H.M. Ortner	Fresenius Journal of Analytical Chemistry 340: 135-139	Single lab
Estimating Detection Limits in Ultratrace Analysis. Part I: The Variability of Estimated Detection Limits	1991	C.L. Stevenson, J.D. Winefordner	Applied Spectroscopy 45:1217-1224	Single lab

Title	Year	Author	Source	Category
Reporting Low-Level Data for Computerized Data Bases	1988	M. Brossman, G. McKenna, H. Kahn, D. King, R. Kiesper, J. Taylor	ACS Symposium Series 361:317-327	Single lab
Detection Limits with Specified Assurance Probabilities	1987	C.A. Clayton, J.W. Hines, and P.D. Elkins	Analytical Chemistry 59: 2506-2514	Single lab
Limit of Detection and Limit of Determination - Application of Different Statistical Approaches to an Illustrative Example of Residue Analysis	1987	J. Vogelgesang	Fresenius Zeitschrift Fur Analytsche Chemie 328: 213-220	Single lab
Determining the Lowest Limit of Reliable Assay Measurement	1983	L. Oppenheimer, T.P. Capizzi, R.M. Weppelman, H. Mehta	Analytical Chemistry 55: 638-643	Single lab
Principles of Environmental Analysis	1983	L.H. Keith, W. Crummett, J. Deegan Jr, R.A. Libby, J.K. Taylor, G. Wentler	Analytical Chemistry 55: 2210-2218	Single lab
Trace Analyses for Wastewaters	1981	John Glaser, Denis Foerst, Gerald McKee, Stephan Quave, William Budde	Env. Sci. & Tech 15: 1426-1435	Single lab
Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry	1980	MacDougall, Daniel, *et al.*	Anal. Chem. 52: 2242-2249	Single lab
Sensitivity and Limit of Detection in Quantitative Spectrometric Methods	1974	J.D. Ingle Jr.	Journal of Chemical Education, 51, 100-105.	Single lab
Decision and Detection Limits for Linear Calibration Curves	1970	A. Hubaux, G. Vos	Analytical Chemistry 42: 849-855	Single lab
Limits for Quantitative Detection and Quantitative Determination	1968	L.A. Currie	Analytical Chemistry 40: 586-593	Single lab
A Statistical Method for Evaluation of Limiting Detectable Sample Concentrations	1967	P.A. St. John, W.J. McCarthy, J.D. Winefordner	Analytical Chem. 39: 1495-1597	Single lab
Initial Evaluation of Quantitative Performance of Chromatographic Methods Using Replicates at Multiple Concentrations	2001	M.A. Castillo, R.C. Castells	Journal of Chromatography A 921: 121-133	Single lab - multilevel
Multivariate Detection Limits with Fixed Probabilities of Error	1999	R. Boque, M.S. Larrechi, F.X. Rius	Chemometrics and Intelligent Laboratory Systems 45: 397-408	Single lab - multilevel
Evaluation of Approximate Methods for Calculating the Limit of Detection and Limit of Quantification	1999	M.E. Zorn, R.D. Gibbons, W.C. Sonzogni	Environmental Science & Technology 33: 2291-2295	Single lab - multilevel
Limits of Detection, Identification and Determination: A Statistical Approach for Practitioners	1998	J. Vogelgesang, J. Hadrich	Accreditation Quality Assurance 3: 242-255	Single lab - multilevel
Weighted Least-Squares Approach to Calculating Limits of Detection and Quantification by Modeling Variability as a Function of Concentration	1997	M.E. Zorn,, R.D. Gibbons, W.C. Sonzogni	Analytical Chemistry 69: 3069-3075	Single lab - multilevel
Detection Limits in GC-MS Multivariate Analysis	1997	Boque R et al.	Quimica Analytica, 16(2), 81-86	Single lab - multilevel
An Alternative Minimum Level Definition for Analytical Quantification	1997	Robert Gibbons, David Coleman, Raymond Maddalone	Environmental Science & Technology 31: 2071-2077	Single lab - multilevel

Title	Year	Author	Source	Category
A Two-Component Model for Measurement Error in Analytical Chemistry	1995	David Rocke, Stefan Lorenzato	Technometrics 37: 176-184	Single lab - multilevel
Practical Quantitation Limits	1992	R.D. Gibbons, N.E. Grams, F.H. Jarke, K.P. Stoub	Chemometrics and Intelligent Laboratory Systems 12: 225-235.	Single lab - multilevel
Experimental Comparison of EPA and USATHAMA Detection and Quantitation Capability Estimators	1991	C.L. Grant, A.D. Hewitt, T.F. Jenkins	American Laboratory 23: 15-33	Single lab - multilevel
High Pressure Liquid Chromatography Determination of the Intermediates Side Reaction Products in FD&C Red No. 2 and FD&C Yellow No. 5: Statistical Analysis of Instrument Response	1978	C.J. Bayley, E.A. Cox, J.A. Springer	J. Assoc. Off. Anal. Chem 61: 1404-1414.	Single lab - multilevel
Method Detection Limits: Application to Organic Environmental Chemistry Data	2002	Wade, T. L., J. L. Sericano, Y. Qian, G. Wolff, and G. Denoux	Presentation at ACS Symposium, Boston, MA, August 2002	Suggested by a peer reviewer
Detection limits	2002	van der Voet, H.	Encyclopedia of Environmetrics, 1, El-Shaarawi, A. H. and Piegorsch, W. W. (eds.), 504-515. Chichester: John Wiley & Sons	Suggested by a peer reviewer
Statistical Approaches to Estimating Mean Water Quality Concentration with Detection Limits	2002	Shumway, R., R. Azari, and M. Kayhanian	Environmental Science and Technology 36: 3345-3353	Suggested by a peer reviewer
Detection Limit of Isotope Dilution Mass Spectrometry	2002	Yu, L. L., J. D. Fassett, and W. F. Guthrie	Analytical Chemistry. 74: 3887-3891	Suggested by a peer reviewer
ISO 17025 Requirements: How to Evaluate Uncertainty for Dioxin Analysis in Food and Feed from Validation Data?	2002	G. Eppe, and E. De Pauw	Proceedings of the 22nd International Symposium on Halogenated Environmental Organic Pollutants and POPs, Barcelona, Spain, August 12-18, 2002, Vol. 59, pp. 403-406, 2002	Suggested by a peer reviewer
Are Target Dioxin Levels in Animal Feedingstuffs Achievable for Laboratories in Terms of Analytical Requirements? Results of an Interlaboratory study	2002	G. Eppe, and E. De Pauw	Proceedings of the 22nd International Symposium on Halogenated Environmental Organic Pollutants and POPs, Barcelona, Spain, August 12-18, 2002, Vol. 59, pp. 407-410, 2002	Suggested by a peer reviewer
Environmental Statistics with S-PLUS	2001	Millard, S. P., and Neerchal, N. K.	Chapman & Hall/CRC, Boca Raton, FL	Suggested by a peer reviewer
Quantifying Uncertainty in Analytical Chemistry	2000	Ellison, S. L. R., M. Roslein, and A. Williams, eds.	EURACHEM/CITAC Guide 2000	Suggested by a peer reviewer
Development and Harmonisation of Measurement Uncertainty Principles. Protocol for Uncertainty Evaluation from Validation Data	2000	Barwick V.J., Ellison S.L.R.	VAM Project 3.2.1	Suggested by a peer reviewer
Statistical Procedures for Analysis of Environmental Monitoring Data & Risk Assessment	1998	McBean, E. A., and Rovers, F. A.	Prentice Hall PTR, Upper Saddle River, NJ	Suggested by a peer reviewer

Title	Year	Author	Source	Category
Foundations and future of detection and quantification limits	1996	Currie, L. A.	Proceedings of the American Statistical Association, Section on Statistics and the Environment, 1-8	Suggested by a peer reviewer
Statistical Methods for Groundwater Monitoring	1994	Gibbons, R. D.	John Wiley & Sons, New York	Suggested by a peer reviewer
Spatial chemostatistics	1994	Cressie, N.	Environmental Statistics, Assessment, and Forecasting, Cothern, C. R. and Ross, N. P. (eds.), 131-146. Boca Raton, FL: Lewis Publishers	Suggested by a peer reviewer
Hypothesis testing with values below detection limit in environmental studies	1994	Slyman, D. J., de Peyster, A., and Donohoe, R. R	Environmental Science & Technology 28: 898-90	Suggested by a peer reviewer
A new approach for accommodation of below detection limit data in trend analysis of water quality	1994	Nagaraj, N. K., and Brunenmeister, S. L	Environmental Statistics, Assessment, and Forecasting, Cothern, C. R. and Ross, N. P. (eds.), 113-127. Boca Raton, FL: Lewis Publishers	Suggested by a peer reviewer
Errors and detection limits	1992	Adams, M. J.	In Methods of Environmental Data Analysis, Hewitt, C. N. (ed.), 181-212. Amsterdam: Elsevier Applied Science	Suggested by a peer reviewer
Statistical inference from multiply censored environmental data	1991	El-Shaarawi, A. H., and Naderi, A	Environmental Monitoring and Assessment 17: 339-347	Suggested by a peer reviewer
Less than obvious: Statistical treatment of data below the detection limit	1990	Helsel, D. R	Environmental Science & Technology 24: 1766-1774	Suggested by a peer reviewer
Environmental tests: Are they valid?	1990	Maynard, A. W.	Chemical Technology 20: 151-155.	Suggested by a peer reviewer
Detection in Analytical Chemistry: Importance, Theory, and Practice	1988	Currie, L. A.	American Chemical Society, New York	Suggested by a peer reviewer

Appendix B
Computation of Detection and Quantitation Limits

INTRODUCTION

This appendix supports the Revised Assessment Document (RAD) for EPA's assessment of detection and quantitation approaches. It presumes that the reader has read chapters three through five of the RAD.

We have compared detection and quantitation limits computed from data gathered by EPA or submitted to EPA by stakeholders commenting on EPA's February 2003 (EPA-821-R-03-005) assessment. The comparison shows that, in general, detection limits derived from a single concentration level such as EPA's MDL are, on average, approximately the same as detection limits derived from similar approaches such as the ACS LOD and LOQ and ISO/IUPAC CRV and MDV, and are approximately three times lower than a single-laboratory variant of ASTM's IDE; and that all quantitation limit approaches, such as EPA's ML, the ACS and ISO/IUPAC LOQ, and a single-laboratory variant of ASTM's IQE, produce quantitation limits that are generally only slightly different.

EPA's Approach to Establishing Detection and Quantitation Limits in Analytical Methods

The Engineering and Analysis Division (EAD) within EPA's Office of Science and Technology develops analytical methods for use in EPA's Clean Water Act (CWA) programs. In developing these methods, EAD first conducts a single-laboratory study in which an MDL and ML are determined followed by multiple single-laboratory studies in which the MDL and ML are either verified or if necessary, revised. If resources, time, and applications of the method warrant, an interlaboratory study is conducted in which the MDL and ML are further verified or, if necessary, revised.

To set an MDL, which is both conservative and achievable by qualified laboratories, we generally select the highest MDL from among the MDLs determined or verified by laboratories in the various studies. For example, EPA determined the MDL in Method 1631 (mercury by cold-vapor atomic fluorescence) as 0.05 ng/L in a single laboratory and revised this MDL to 0.2 ng/L based on multiple single-laboratory studies. All laboratories verified the MDL of 0.2 ng/L in an interlaboratory study. Unlike a single-lab MDL and ML computed in a laboratory quality-control setting, the interlaboratory MDL established during method development is set as a high-biased estimate of Currie's Lc. Thus, the single-lab MDL and resulting ML, when scaled up with the interlaboratory MDL data, are very conservative. This interlaboratory scaling up protects against unrealistically low values, and responds to concerns that the MDL is a single-laboratory approach that produces unrealistically low MDLs.

DETECTION AND QUANTITATION LIMITS ASSESSED

EPA used several datasets to evaluate various approaches to determining detection and quantitation values. These data are described in the Data section of this Appendix.

In the original Assessment Document (EPA, February 2003), four different detection and three different quantitation limits were evaluated and compared. The detection limits were the EPA method

detection limit (MDL), the International Standards Organization/International Union of Pure and Applied Chemistry (ISO/IUPAC) critical value (CRV) and minimum detectable value (MDV), and a single-laboratory variant of the ASTM interlaboratory detection estimate (IDE). The quantitation limits were the EPA minimum level of quantitation (ML), the ISO limit of quantitation (LOQ), and a single-laboratory variant of the ASTM interlaboratory quantitation estimate (IQE).

Several stakeholders commenting on EPA's assessment of data expressed difficulty in replicating EPA's calculations supporting these evaluations. Based on these comments, EPA reviewed the computer programs used to calculate the various limits, and compared results obtained using these programs to calculation results and software packages submitted by commenters. EPA concluded that many of the discrepancies between EPA and commenter calculations were due to differences in the datasets and software used (see Software Comparison, later in this appendix). As a result of this review, EPA did, however, find some discrepancies which have been resolved in this document. Revisions are listed below:

- In calculating the single-laboratory IDE (SL-IDE) and single-laboratory IQE (SL-IQE) based on the Exponential model using the Episode 6000 and Method 1631 and 1638 validation study data, incorrect weights were used when modeling recovery. Because the majority of the SL-IDEs were calculated using this model, most of the SL-IDEs presented in Tables 2, 6, 7 and 8 have changed. Because the SL-IQEs were not calculated based on the exponential models, these values did not change.

- When calculating MLs based on the Episode 6000 data, the resulting ML was incorrectly rounded up for many analytes. This has been corrected, and many of the calculated MLs in Tables 4 and 5 have changed.

- In the 2003 assessment, blank results were included in the calculations of the ISO/IUPAC CRV, MDV and LOQ. Upon further review, it was decided that it was invalid to use blank results included in the Episode 6000 study, because these blanks were used to assess carry-over, and would not be representative of routine blank analyses. Therefore, the ISO/IUPAC limits were re-calculated using the lowest spike concentration in place of blank results.

- For two analytes in the Episode 6000 data (uranium and thallium by Method 200.8), incorrect formatting caused multiple spiking levels to be combined improperly. This affected the calculation of all limits for these analytes. This calculation has been fixed, and the limits have changed slightly for these two analytes.

- After completion of the Original Assessment Document, a new version of the IDE procedure (D6091-03) was published by ASTM. This procedure included the use of a standard deviation bias correction factor which was not included in the prior version (D6091-97). Therefore, all IDEs calculated using the Episode 6000 and Methods 1631 and 1638 validation study data were re-calculated using this correction factor. For the majority of analytes, the resulting IDEs increased slightly (by approximately 4%).

The effect of these changes on the analyses are discussed in the Results of Computations section of this Appendix. To better explain how calculations were run, Appendix C gives example calculations of the SL-IDE, SL-IQE, MDL and ML for one analyte.

Along with comments on EPA's assessment, both the American Council of Independent Laboratories (ACIL) and USGS submitted data and procedures. ACIL submitted a procedure for calculating a critical level (CRV) and Long-Term MDL (LTMDL). USGS submitted its procedure for calculating a long-term MDL (USGS LT-MDL). Both the ACIL critical level and USGS LT-MDL are estimates of Currie's Lc, and are therefore comparable to the EPA MDL. Both the ACIL and USGS procedures, however, are based on results collected over a long period of time. The ACIL critical level is based on blank results, and the USGS LT-MDL is based on spiked results. The formula for the ACIL critical level is identical to that of EPA's MDL, except that the mean of the blanks is added to the product of the standard deviation and t-statistic. The USGS procedure does not use a sample standard deviation, but instead uses a non-parametric estimate of variability that is based on the interquartile range. The USGS LT-MDL procedure also allows addition of the mean or median of blank results to the LT-MDL.

ACIL also suggested a separate CRV procedure (ACIL "Case 2") for calculating estimates for those methods for which analysis of blank samples does not produce a signal. For these methods, ACIL suggested an iterative procedure that first determines the lowest level at which all 7 replicates are detected, and then estimates the CRV as the lowest of the observed results of 7 spikes. The analogue of Currie's Ld is estimated as this lowest spike level. EPA finds merit in the idea of dividing the methods into two groups (depending on the presence or absence of a signal from analysis of blank samples) and in the idea of estimating the detection level of the instrument, and plans to further investigate the ACIL approach. However, the particular implementation of the ACIL Case 2 procedure has some conceptual problems that precluded it from evaluation at this time. These problems are described later in this Appendix (see "Episode 6000 Data").

EPA provides further discussion of these approaches and the Agency's reasons for selecting them in Chapters 1 and 2 of the RAD.

Commonality of Approaches

The EPA, ACS, and ISO/IUPAC approaches are all multiples of the standard deviation of either replicate measurements of a blank or of the lowest spike concentration that produces positive (non-zero) results for all 7 replicates. Similarly, the ACIL and USGS approaches are based on multiples of a parametric or nonparametric estimate of variability of replicate measurements, with the difference that the given estimate includes greater sources of variability than those of the other single-concentration approaches.

Other subtle distinctions are that (1) ISO/IUPAC suggest a false positive rate of 5 % ($\alpha = 0.05$) for the CRV and MDV, whereas EPA specifies a false positive rate of 1 % ($\alpha = 0.01$) for the MDL and (2) the EPA MDL was calculated by pooling data from two concentration levels after determining that the variabilities of the two concentration levels are not significantly different (as provided as an option in step 7 of the MDL procedure), thereby increasing the degrees of freedom to 12 from the 6 used in computation of the ISO/IUPAC CRV and ACS LOD. The consequence of distinction (1) is that an approach with a higher allowed false positive rate ($\alpha = 0.05$) will produce a lower detection limit than an approach with a lower false positive rate ($\alpha = 0.01$). The consequence of distinction (2) is that a detection limit resulting from pooling at two levels will be more stable and likely somewhat lower than a detection limit at a single level (given the same variability at each level) because the degrees of freedom are increased in the t statistic.

The ACS and ISO/IUPAC approaches specify replicate measurements of blank samples. In computing detection and quantitation limits from the Episode 6000 data, blank results were not used, as blanks analyzed in this study included carry-over effects, and were therefore not representative of routine blank results. Therefore, the lowest spike concentration (or, in the case of the MDL, two lowest spike concentrations) that produced a non-zero result was used for computation of all approaches. This simplification condensed the EPA MDL and the ACS LOD to a single approach subsequently termed the EPA/ACS DL. Similarly, the EPA ML and ACS LOQ were condensed to a single approach, termed the EPA/ACS QL.

The remaining single-concentration approaches are the ISO/IUPAC CRV, MDV, and LOQ, the ACIL critical level and the USGS LT-MDL. The ISO/IUPAC CRV differs from the EPA/ACS DL because of its suggested use of a false positive rate of 5% ($\alpha = 0.05$) versus use of a false positive rate of 1% ($\alpha = .01$) in the EPA/ACS DL. The ISO/IUPAC MDV also differs from the EPA/ACS DL because of (1) its suggested use of a false positive rate of 5% ($\alpha = 0.05$), (2) its stated false negative rate of 5 % (β=0.05), and (3) recovery correction (estimated using a linear regression). Therefore, the ISO/IUPAC CRV and MDV were each treated separately (were not combined with the EPA or ACS approaches) from the other detection limit approaches in the data analysis. The ISO/IUPAC LOQ is also different from the other quantitation limit approaches and was treated separately from these approaches. The ACIL critical level differs from the EPA/ACS DL in its inclusion of long-term variability and the addition of the mean blank result to the limit. The USGS LT-MDL differs from the EPA/ACS DL in its inclusion of long-term variability, the addition of the median or mean blank result to the limit, and the use of a nonparametric estimate of variability in place of the sample standard deviation. Because of the lack of long-term variability and representative blank results in the Episode 6000 data, the ACIL critical level and USGS LT-MDL could not be calculated using the Episode 6000 data. Assessments of these approaches in comparison to the EPA/ACS DL were done using blank and spiked sample data that were submitted to the Agency by ACIL and USGS.

The ASTM IDE and IQE were treated separately because they are constructed by fitting a model to variability versus concentration data, rather than being derived from the standard deviation of replicate measurements of a single concentration, (as are the EPA, ACS, ISO/IUPAC and ACIL approaches). Similar to some of the ISO/IUPAC approaches, the ASTM IDE and IQE include "protection" against false negatives and recovery correction (see section 3.3 of the Revised Assessment Document for a discussion on EPA's concerns about false negative protection). The IQE, but not IDE, also includes an added correction for the bias associated with an estimate of the true standard deviation at each concentration. In the context of the IQE, the word "bias" means the amount by which the estimated sample standard deviation is low compared to the true population standard deviation, and should not be confused with common use of the word "bias" in an analytical measurement.

Single-laboratory Variants of Interlaboratory Approaches

Because the EPA, ACS, and ISO/IUPAC approaches are single-laboratory approaches, and the ASTM IDE and IQE are interlaboratory approaches, the ASTM approaches could not be computed using the single-laboratory data in the Episode 6000 studies. To solve this problem, single-laboratory variants of the IDE and IQE were used. These single-laboratory variants were termed the SL-IDE and SL-IQE for "single-laboratory IDE" and "single-laboratory IQE," respectively. The SL-IDEs and SL-IQEs were constructed using the overall standard deviation within a single laboratory at each concentration rather than the overall standard deviation across all laboratories at each concentration.

Attempted Application to Interlaboratory Data

EPA attempted to apply the various approaches to interlaboratory study data in response to a request by the Petitioners to the Settlement Agreement and so that detection and quantitation limits could be compared. However, because the EPA, ACS, and ISO/IUPAC approaches are single-laboratory approaches, whereas, the ASTM approaches are interlaboratory approaches, it was not possible to compute directly comparable detection and quantitation limits from the same data.

It was possible, however, to compare the detection and quantitation limits produced by EPA and the Electric Power Research Institute (EPRI) from the EPA Method 1631 and EPA Method 1638 interlaboratory study data. Although the resulting detection and quantitation limits are either single-laboratory (EPA) or interlaboratory (ASTM), as appropriate to the particular approach, a comparison of the resulting limits can be informative. The EPRI detection and quantitation limits are presented in EPRI reports of the results of the Method 1631 and Method 1638 studies.

DATA

Datasets Evaluated

The datasets used to evaluate the detection and quantitation approaches discussed above are described in this section. EPA computed EPA/ACS DLs and QLs; ISO/IUPAC CRVs, MDVs and LOQs; and single-laboratory variants of ASTM IDEs (SL-IDEs) and IQEs (SL-IQEs) using the Episode 6000 data. EPA also computed IDEs and IQEs for the Method 1631 and 1638 interlaboratory study data. EPA computed ACIL's critical level, USGS's LT-MDL and EPA's MDL based on a combination of blank and spiked data submitted by USGS, and performed an assessment of the effect of long-term variability based on blank data submitted by ACIL.

EPA's Variability versus Concentration Studies ("Episode 6000")

In 1997 and 1998, EPA conducted a study of variability vs. concentration for a number of analytical methods. Six laboratories were employed for the analyses; each analyte and method combination was tested by one of these laboratories. For nearly all of the technologies, the studies were conducted by spiking reagent (i.e., blank, presumably "clean") water at 16 different concentrations per analyte, ranging from 100 times an initial estimate of the MDL to 0.1 times the initial estimate. A total of 198 analytes were measured, generally with seven replicates analyzed at each concentration. Details of the study design are described in EPA's *Study Plan for Characterizing Variability as a Function of Concentration for a Variety of Analytical Techniques* (July 1998), and in Appendix C of the February 2003 Assessment document. Based on the sampling episode number assigned to the study by the EPA Sample Control Center, the study and results have become known as the Episode 6000 study and data.

The analytes and analytical techniques studied were:

- Total suspended solids (TSS) by gravimetry
- Metals by graphite furnace atomic absorption spectroscopy (GFAA)
- Metals by inductively-coupled plasma atomic emission spectrometry (ICP/AES)
- Hardness by ethylene diamine tetraacetic acid (EDTA) titration
- Phosphorus by colorimetry

- Ammonia by ion-selective electrode
- Volatile organic compounds by purge-and-trap capillary column gas chromatography with a photoionization detector (GC/PID) and electrolytic conductivity detector (GC/ELCD) in series
- Volatile organic compounds by gas chromatography with a mass spectrometer (GC/MS)
- Available cyanide by flow-injection/ligand exchange/amperometric detection
- Metals by inductively-coupled plasma spectrometry with a mass spectrometer (ICP/MS)

EPA's 2003 assessment of detection and quantitation examined a dataset populated with the results of this study, the object of which was to characterize analytical variability as a function of concentration over a wide range of concentrations, analytes, and analytical methods. Data from this study, including many tables and plots, were provided in the record supporting EPA's original assessment and discussed in EPA's "Technical Support Document for the Assessment of Detection and Quantitation Approaches," EPA 821-R-03-005, February 2003. The database developed contains a total of approximately 22,000 data points. This study was conducted in contract laboratories. EPA performed a contract compliance review of these studies at the time the studies were conducted, but not a point-by-point review of each of the tens of thousands of data points.

In the study, an initial (range finding) MDL was determined for each combination of analyte and analytical technique using a revised draft of the MDL procedure. The revised draft had three significant changes: (1) the definition was more closely conformed to the MDL procedure; (2) optional iterative step 7 of the MDL procedure was made mandatory; and (3) the spike concentration to MDL was reduced from 5 to 3 in an attempt to narrow the resulting MDL. During data gathering, two laboratories complained that the reduction in spike to determined MDL ratio (from 5 to 3) caused a large number of iterations and stated that 5 was more reasonable. Subsequently, EPA returned to the spike to MDL ratio of 5 published in the 40 CFR 136, Appendix B procedure.

After determining the initial MDL, each laboratory analyzed 7 replicates of samples spiked at concentrations of 100, 50, 20, 10, 7.5, 5.0, 3.5, 2.0, 1.5, 1.0, 0.75, 0.50, 0.35, 0.20, 0.15, and 0.10 times the initial MDL. In a few instances, laboratories analyzed more than 7 replicates. Results associated with the replicate analyses at each concentration level were obtained, as often as possible, using the same calibration that was used in determining the initial MDL. Where laboratory reports indicated that multiple calibrations were conducted, the association between each result and its calibration was used in the data analysis.

Spiked aqueous solutions were analyzed in order from the highest concentration (100 times the MDL) to the concentration at which 3 or more non-detects (zeros) were encountered among the 7 replicates, or the lowest concentration specified (0.1 times the MDL), whichever occurred first. This analysis order (1) minimized carryover that could occur in some methods if a low-concentration sample had followed a high-concentration sample (as may happen when samples are analyzed in random order), and (2) prevented collection of a large number of zeros if the signal disappeared.

A variant of the iterative MDL procedure was used for organic compounds determined by chromatographic methods. Methods for organics normally list many (15 to 100) analytes, and the response for each analyte is different. Therefore, to determine an MDL for each analyte, the concentration of the spike would need to be inversely proportional to the response. Making a spiking solution with 15 to 100 different concentrations is cumbersome and error prone. The approach used in the study was to run 7 replicates at decreasing concentrations until signal extinction, then select the

concentration(s) appropriate for the MDL for each analyte according to the MDL procedure. In some cases the laboratories selected the concentrations, in others cases, EPA did. This approach was generally applied for organics analysis. However, laboratories also had the option of using some combination of monotonically decreasing concentrations described above and a few selected concentrations to achieve the desired spiking levels.

Some commenters on the 2003 assessment noted possible errors. EPA reviewed these comments and examined the individual data values and other aspects of the assessment that commenters thought were in error. Commenters commented most frequently on measurements of organic compounds by EPA Methods 502.2 (halogenated and aromatic volatiles by GC with photoionization and electrolytic conductivity detectors in series) and 524.2 (volatiles by GC/MS) that were included in the Episode 6000 dataset. EPA performed a more comprehensive review of these data points, and found that the calculated recoveries of some of the compounds are higher or lower than would be expected for the analytical technologies employed. There also appear to be low background concentrations of some compounds in the reagent (blank) into which the analytes were spiked. Backgrounds are commonly observed in determinations of metals, radionuclides, and some volatiles.

Without the raw data for the analyses in question, it is not possible to unequivocally determine the root cause(s) of the high or low recoveries and possible backgrounds. However, atypical recoveries may have been the result of (1) laboratories making measurements at levels as much as 50 times below the lowest level to which they would normally calibrate to establish MDLs and MLs at as low a level as could be measured, and (2) EPA's request that the laboratories use a single calibration (rather than multiple) to prevent discontinuities in the variability vs concentration trends that were the object of these studies.

Another possible explanation for the low apparent recoveries is the setting of thresholds in the GC and GC/MS analyses. If a small constant area of a GC response peak is removed by thresholding, the relative amount of area that is removed will increase as the concentration is reduced, resulting in lower apparent recoveries at the lower concentrations. This effect would be consistent with observations in some of the data.

As for possible backgrounds for volatiles or metals, these backgrounds likely were either present in the reagent (blank) water used by the laboratories for the MDL determinations, or by carry-over from one sample to another. To test for carry-over, some laboratories analyzed one or more blank sample between spike levels after verification of calibration. Instances in which multiple blanks were analyzed often show decreasing small concentrations for some of the analytes. However, these backgrounds resulting from carry-over mean that blank results should not be used to assess false positive rates of the different limits calculated using the Episode 6000 data.

Interlaboratory Study Data

EPA used data from two interlaboratory method validation studies to calculate IDEs and IQEs for a total of 10 metal analytes. These studies were conducted by EPA to evaluate performance of EPA Methods 1631 and 1638, and to gather data to evaluate existing performance specifications, including detection and quantitation limits. To expand the scope of the study, the Electric Power Research Institute (EPRI) funded the distribution of additional samples to study participants. Each study included multiple participant laboratories: twelve for Method 1631 and eight for Method 1638.

The two studies were designed so that each participating laboratory would analyze sample pairs of each matrix at concentrations that would span the analytical range of the method. Each laboratory was provided with multiple sample pairs, including samples measured in filtered effluent, unfiltered effluent, marine water, filtered freshwater, and spiked reagent water. Each laboratory analyzed reagent water sample pairs for each analyte at five different concentration levels. The results of the reagent water analyses were used to fit variability functions and calculate IDEs and IQEs.

Data from these studies also are discussed in Chapter 1 of this document.

Data Submitted by Stakeholders

EPA also used datasets containing results from analysis of blank samples provided by two stakeholders. Blanks analyzed over a period of three months for five analytes using Method 200.7 were provided by the American Council of Independent Laboratories (ACIL), while blanks analyzed over a period of one year representing 78 analytes were provided by the US Geological Survey (USGS). In addition to these blank results, USGS sent results of the analyse of spiked samples representing 39 analytes. Because spiked samples were analyzed only at a single concentration level, many of the different detection and quantitation limits, such as the SL-IDE and SL-IQE, cannot be calculated using these data. However, a comparison of the critical level suggested by the ACIL, the LT-MDL suggested by USGS, and the EPA MDL was performed using the blank and spiked results.

The data submitted by ACIL and USGS also are discussed in Chapter 1 of this document.

Datasets Not Evaluated

The Petitioners and Intervenor to the Settlement Agreement provided the list of datasets shown in Table 1 and suggested that EPA evaluate detection/quantitation limit approaches using the datasets on the list. However, in reviewing the datasets suggested, EPA determined that many were developed for characterizing the behavior of an analyte or analytes across the analytical range of a method, rather than in the region of detection and quantitation. For example, any dataset developed prior to the advent of the IDE and IQE would be inappropriate because there could not have been an estimate of IDE_0 or IQE_0 (i.e., an initial estimate of the given limit; see Section 6.2.2.1 of D6091 and D6512). This eliminates all datasets in Table 1 except the EPA/EPRI Method 1631, the EPA/EPRI Method 1638 dataset, and the MMA 2001-2 dataset. It is possible that some spike level in one or more of the datasets developed prior to the advent of the IDE and IQE would fortuitously meet the IDE/IQE criteria. But the IDE and IQE can be circular; i.e., once developed from a given dataset, there may be a spike level in the dataset that can be construed to meet the criteria. Datasets developed without following the IDE and IQE procedures, particularly without making an *a priori* estimate of IDE_0 or IQE_0, do not meet the requirements of the IDE and IQE procedures, regardless of whether the data in them can be construed to have met those requirements after the fact.

In addition, these datasets do not lend themselves to the comparisons used in this report because the developers of these datasets did not apply the measurements needed to establish an MDL and ML. Therefore, MDLs and MLs could not be determined for comparisons (see the section titled "EPA's Approach to Establishing Detection and Quantitation Limits in Analytical Methods").

The EPA 6000 dataset is comprehensive in coverage of analytes, analytical techniques, and a concentration range from 0.1 to 100 times the MDL, whereas the datasets suggested by Petitioners focus on metals, two Aroclors, and concentrations across the analytical range of the method. The range of data used for construction of an IDE or IQE is particularly important. As detailed in the discussion of the "Effect of number and spacing of concentrations for determination of the SL-IDE and SL-IQE" below, including data across the analytical range in calculation of an SL-IDE significantly raises the SL-IDE.

After EPA published the February 2003 Assessment Document for comment, three commenters offered to provide EPA with additional data that would enhance EPA's assessment. EPA requested the data offered by each of these organizations, but received a response from only two of the three (an analytical laboratory and USGS). After evaluating these data, EPA determined that the data from the analytical laboratory were not useful because they were limited to calibration data and did not include the data from extraction that is needed to compare detection/quantitation approaches.

Michigan Manufacturers Association (MMA) Dataset

In March of 2002, John Phillips of Ford Motor Company submitted a report of results from a study of two Aroclors (PCBs) by the Michigan Manufacturers Association (MMA) for EPA's consideration in evaluating detection and quantitation limit approaches. EPA did not use this dataset because of problems, such as the dataset was limited to a maximum number of five analytical results per spike level, which is inconsistent with the minimum number of seven analytical results per spike level required for determining an MDL, and other values that are determined using non-ASTM approaches. In comments on EPA's evaluation, Hunton and Williams (a law firm representing the Inter-industry Analytical Group), stated that EPA should not have excluded the MMA dataset from its assessment of detection and quantitation approaches. EPA notes, however, that because of the insufficient number of analytical results, comparison of various detection and quantitation approaches is not possible with this dataset, and has not included the dataset in this evaluation. In addition, MMA samples spiked with low levels of PCBs as Aroclors produced an average recovery on the order of 500% at the lowest spike concentration whereas PCBs are recovered at approximately 80% from water in this concentration range (see the recovery data in EPA Methods 608 and 1668A). A logical explanation for the 500% recoveries in the MMA study is that the samples were contaminated by the sample preparation laboratory, by many of the participant laboratories, or both. A single and simple test, which was not conducted in the MMA study, of an aliquot of the prepared water samples using a method, such as EPA Method 1668A, would have demonstrated that the samples were free from contamination and contained the stated spike concentrations at the time that the samples were prepared.

COMPUTATIONS

All computations were carried out using Statistical Analysis System (SAS) version 8.01. The equations for all approaches were programmed into the SAS software by a senior statistician, with assistance from senior analysts. There is some ambiguity in the IUPAC/ISO and ASTM detection and quantitation limit approaches and in interpretation of results from the ASTM approaches. Several formulas are given in the IUPAC/ISO documentation, but none are defined to be the official ISO/IUPAC detection and quantitation limit approaches. Therefore, calculations for the CRV, MDV, and LOQ were chosen because they were most representative of Lloyd Currie's definitions of a critical value, detection

limit and quantitation limit. Ambiguity in results from the ASTM approaches is attributable to the subjective nature of interpreting residual plots for each analyte. To resolve this issue, IDE and IQE models were chosen using significance tests for slope and curvature.

References used for the IUPAC/ISO approaches were those published by Currie in *Pure and Applied Chemistry* **67**:10, 1699-1723 (1995) as updated by *Analytica Chimica Acta* **391** 105-126 (1999). Where needed, the ASTM approaches were programmed as single-laboratory variants of the Practices D 6091 (IDE) and D 6512 (IQE). EPA has included the SAS program code on the CD-ROM that supports this document.

To assess stakeholder comments about calculations of the IDE and IQE that were performed and summarized in the original assessment document, EPA requested additional software packages offered by commenters who use the software to determine these limits. On April 20, 2004, EPA received copies of two software packages written for the purpose of determining the IDE and IQE from a representative of Ford Motor Company. The first of these is Qcalc (version 1.0), a DOS-based program. The second of these is an Excel spreadsheet which utilizes Excel functions, macros and an add-in function to determine IDEs and IQEs. These two programs were compared to the SAS programs used by EPA by calculating IDEs and IQEs based on a subset of the Episode 6000 dataset. The results of this comparison are described later in this Appendix (see section titled "Comparison of IDE/IQEs Calculated Using Different Software Packages").

Calculation of the ACIL CRV, USGS LTMDL, and EPA MDL was done using analytical results of blank and spiked samples submitted by USGS. Specific details of these calculations are described in the section titled "USGS Blank and Spiked Metals and Nutrient Data" later in this Appendix.

RESULTS OF COMPUTATIONS

Detection and quantitation limits are presented in a set of tables corresponding to the Episode 6000 study, a single table corresponding to the Method 1631 and Method 1638 studies, and a single table summarizing limits calculated using data submitted by USGS. Within the Episode 6000 dataset, results for detection limits are compared followed by results for quantitation limits. Within the comparison of limits (detection or quantitation), the first table compares the actual limits followed by a table of percent differences between limits.

Episode 6000 data

Table 2 compares detection limits produced by four approaches (EPA/ACS DL; ISO/IUPAC CRV; ISO/IUPAC MDV; and ASTM SL-IDE) and Table 3 presents the percent difference between these approaches, using the formula given below:

$$\%\ difference = \frac{(Lim - DL)}{(Lim + DL)/2} * 100\%$$

where: DL is the EPA/ACS DL for the given analyte, and
Lim is the corresponding limit (CRV, MDV, or SL-IDE) being compared to the DL.

The median percent difference between the EPA/ACS DL and each of the other three limits was compared to 0% using two significance tests: the sign test and Wilcoxon rank-sum test. The sign test evaluates whether the given limit exceeds the EPA/ACS DL 50% of the time. The Wilcoxon rank-sum test is a more powerful test which, unlike the sign test, takes into account the magnitude of the difference between the two limits by ranking the percentage differences presented in Table 3.

The ISO/IUPAC CRV was less than the corresponding EPA/ACS DL for 97% of the analytes and methods, with a median percent difference of -35.7%. The median percent difference of ISO/IUPAC CRV to EPA/ACS DL was significantly less than 0% based on both the sign and Wilcoxon tests with α = 0.05 ($p<0.0001$ for both tests). The major reason for this difference is most likely the different Type I error rate for the two approaches (α = 0.01 for the EPA/ACS DL and α = 0.05 for the ISO/IUPAC CRV).

The median percent difference between the ISO/IUPAC MDV and the EPA/ACS DL is 8.8% with the MDV exceeding the DL for 53% of the analytes. The median percent difference between the ISO/IUPAC MDV and EPA/ACS DL did not differ significantly from 0% based on the sign test ($p=0.523$) or the Wilcoxon rank-sum test ($p=0.164$) with α = 0.05. The likely reason that the two approaches do not yield significantly different results is that the correction for false negatives and recovery correction in the MDV (β = 0.05) are counteracted by the smaller Type I error rate for the EPA/ACS DL.

The median percent difference between the ASTM SL-IDE and the EPA/ACS DL is 108.7%; i.e., the single-laboratory variant of the ASTM IDE is, on average, three times as large as that of the EPA and ACS approaches. The SL-IDE was greater than the corresponding EPA/ACS DL for 92% of the analytes and methods. The median ratio differed significantly from 1, based on both the sign and Wilcoxon tests with α = 0.05 ($p<0.0001$ for both tests). The median ratio and percent of SL-IDEs exceeding the corresponding EPA/ACS DL both increased slightly compared to the calculations presented in the original assessment document, due to the correction of the exponential model calculations for the SL-IDE and the use of the standard deviation bias correction. It is not surprising that the SL-IDE results were generally greater than the EPA/ACS DL, as the SL-IDE is an estimate of Currie's L_D, whereas the EPA/ACS DL is an estimate of Currie's L_C. In addition, the use of two tolerance interval limits in the IDE calculation likely also led to the large difference between the SL-IDE and EPA/ACS DLs.

Table 4 compares quantitation limits produced by the three approaches (EPA/ACS QL; ISO LOQ; and ASTM SL-IQE) and Table 5 compares the percent difference between these approaches taking the EPA/ACS QL as reference. Similarly to the detection limit approaches, the median percent difference was compared to 0% using the sign and Wilcoxon tests. The median percent difference between the ISO/IUPAC LOQ and the EPA/ACS QL is -4.2%, and the median percent difference between the ASTM SL-IQE and the EPA/ACS QL is 19.6%. The ISO LOQ and ASTM SL-IQE are greater than the corresponding EPA/ACS QL for 47% and 62% of the analytes and methods, respectively. The median ratio between the LOQ and QL did not differ significantly from 0% based on the sign test ($p=0.390$), but did based on the Wilcoxon test ($p=0.043$) at α=0.05. The median ratio between the SL-IQE and QL differed significantly from 0% based on both the sign test ($p=0.001$) and the Wilcoxon test ($p<0.0001$).

For the SL-IQE comparisons, this result is different from those presented in the original assessment document, due to the fixed rounding issue in the ML calculations (see discussion under Detection and Quantitation Limits Assessed). Because the EPA/ACS QL and the SL-IQE are both estimates of Currie's L_Q, the reason for this difference is not clear. One possible reason for this significant difference is that the SL-IQE does not assume that variability at the quantitation limit is equal to variability of the blank, whereas the EPA/ACS QL does. However, it is worth noting that the difference seems to be strongly affected by which model was used to calculate the SL-IQE. The median percent difference between the QL and SL-IQE is -7.7% when the hybrid model is used to calculate the SL-IQE compared to 67.9% and 179.6% for the linear and constant models, respectively. While use of the constant model assumes that the variability is constant between the blank and quantitation limit, this model type is generally chosen only when there are unusually high results at one or more of the lower spike levels for a given analyte. Therefore, the SL-IQEs calculated for these analytes are likely somewhat biased high.

Although the Episode 6000 dataset is not ideal for evaluating the ACIL Case 2 iterative approach for those methods/instruments for which analysis of blank samples does not produce a signal, EPA estimated the ACIL Case 2 CRV using the lowest concentration level at which all 7 replicates were observed to test if the conceptual problem with ACIL's implementation of Case 2 occurs in practice. EPA noticed that, because the estimate of Currie's L_C is based on measured values and the estimate of Currie L_D is based on spike level, the estimate of L_D could theoretically fall below L_C for methods with recovery that systematically exceeds 100% or for data with some contamination. Looking at Episode 6000 data, EPA confirmed that this problem may occur in practice. In fact, it occurred for 35 of the 146 analytes (24%) measured using methods that do not always result in signals from analysis of blank samples.

EPA/EPRI Method 1631 and 1638 Interlaboratory Method Validation Study Data

Table 6 compares detection and quantitation limits computed from data generated in the Method 1631 and Method 1638 interlaboratory studies. MDLs and MLs are those listed in EPA Methods 1631 and 1638. EPA computed IDEs and IQEs for the purpose of preparing this assessment. IDEs and IQEs computed by EPRI are from the EPRI reports on the Method 1631 and Method 1638 interlaboratory studies.

In reviewing these data, it must be recognized that the EPA MDLs and MLs are the result of selecting the highest MDL in EPA's single-laboratory studies or interlaboratory study, whereas the IDEs and IQEs are the result of a statistical process that includes recovery correction, correction for bias in the sample standard deviation (IQE only), allowance for prediction and tolerance intervals, interlaboratory variability, and model selection. The most significant reason for the instances of a large disparity between the EPA-determined IDEs/IQEs and the EPRI-determined IDEs/IQEs is model selection. EPA selected the model based on a strict application of the IDE and IQE procedures by a senior statistician. For those instances in which EPA and EPRI selected the same model, the IDEs and IQEs are nearly the same.

Table 7 compares IDEs and IQEs resulting from the four main model types described in the ASTM IDE and IQE procedures. IDEs and IQEs resulting from the constant model were the highest for all analytes. IDEs and IQEs resulting from the other three models were almost equal for some analytes (lead, for example), and differed by more than an order of magnitude for others (mercury, for example). For two analytes, the IDE and IQE estimated using the linear model were negative. This was due to a negative intercept estimate in the precision model. The ASTM IDE and IQE procedures dictate that the linear model should not be used in this situation.

Table 7 also includes RSDs between the IDEs and IQEs calculated using the different model types. This was done based on commenter statements that the choice of model had only a minimal effect on the resulting IDE or IQE. This analysis is discussed later in this Appendix (see "Comparison of IDE and IQEs calculated using Different Models").

USGS Blank and Spiked Metals and Nutrient Data

USGS supplied EPA with blank data collected over a period of one year for 78 metals and nutrient analytes and spiked data collected over a period of one year for 39 metals and nutrient analytes. These results were used to calculate both the USGS LT-MDL and ACIL critical level. The ACIL critical level was calculated using the blank results for the given analyte and method. The USGS LT-MDL was calculated based on the spike results for the given analyte and method. In addition, the LT-MDL was calculated in two ways: by adding the mean of the blank results for the given analyte and method, and by adding the median of the blank results for the given analyte and method.

The EPA MDL also was calculated for each analyte/method using the spiked sample results provided by USGS. Because MDLs are typically calculated using fewer replicates than the 15 to 24 analyzed by USGS, EPA calculated the MDL by simulating different subsets of 7 replicates. Subsets were created by taking each set of 7 consecutive spiked results, i.e., the first 7 samples analyzed would be one subset, the 2nd through 8th samples analyzed would be another subset, etc. This yielded a total of n-6 subsets, where n is the number of total samples for that analyte. The MDL was then determined by randomly choosing one of the n-6 subset MDLs. While the use of only seven replicates run consecutively in each subset minimized the effect of long-term variability, it is worth noting that the amount of temporal variability in each subset is still greater than that typically included in the EPA MDL (i.e., MDL datasets typically are generated in a single day); the time interval between the first and last replicate analyzed within a subset ranged from 30 to 48 days. Therefore, the calculated MDLs are likely somewhat higher than those that would be calculated using results generated over a single day.

After calculation of these limits, the percentage of blank results included in the dataset that exceed each limit for each analyte was calculated. Because all limits were calculated at the 99% confidence level, it would be expected that the average percent of blanks exceeding each limit would be approximately 1% when the blank results follow a Normal distribution centered at 0. Limits based on each of the calculations are presented in Table 10.

Generally, the percentage of blanks exceeding the ACIL critical level was lower than the percentage exceeding the other limits (see summary table following Table 10). The percentages of blanks exceeding the EPA MDL were slightly higher compared to the percentages exceeding the ACIL critical level, due to a small subset of analytes with notable blank bias. The USGS LT-MDL had higher rates of blank exceedance than either the ACIL or EPA limits, regardless of whether the mean or median was added to the limit. This suggests that the effect of blank bias was smaller than the effect of the method of estimating variability. USGS uses the nonparametric calculation to lessen the effect of outliers on the estimate of variability. Because those blanks that exceed a given limit are likely to be outliers themselves, this can lead to inflated exceedance rates. However, it is worth noting that, for the majority of analytes where blanks exceeded the calculated USGS limits, multiple blank results were greater than the associated limit. This suggests that some non-outlying blank results also are exceeding the USGS limits for some analytes.

DISCUSSION

Negative detection limits for the ISO/IUPAC MDV

The calculated ISO/IUPAC MDV was negative for 29 analytes in the Episode 6000 data. Negative MDVs are attributable to the use of a regression model to estimate recovery at each concentration. The standard errors and correlation of the regression parameters are included in the calculation of the MDV. Analytes for which the MDV was negative seemed to coincide with an unusually large standard error of the regression intercept, which generally occurred when the estimated intercept was strongly negative. The large standard error of the intercept was likely due to extrapolating the recovery model to zero concentration; the error around a regression line is greatest for concentrations furthest away from the mean spike level. The effect of this extrapolation also may be seen in the Episode 6000 data. No negative results were used in the MDV and LOQ calculations, yet the median recovery intercept for the analytes analyzed in the Episode 6000 dataset was equal to -0.11. The standard errors of the intercept and slope estimates were generally high (intercept median= 0.27, slope median=0.011), and therefore the estimated intercept and slope terms were frequently not significantly different from 0 and 1, respectively (intercept: not different from zero for 167 analytes/methods; slope not significantly different from 1 for 106 analytes; both intercept and slope not significantly different for 79 analytes). Because the recovery model parameters are not significantly different from 0 or 1 for the majority of analytes, and both the estimated slope and the standard errors of the slope and intercept are included in the calculation of the MDV and LOQ, the inclusion of the recovery model estimates may bias the calculated limits, to the point that the resulting MDV can be negative.

Effect of number and spacing of concentrations for determination of the SL-IDE and SL-IQE

Tests in the Episode 6000 studies were conducted at 16 concentration levels. The IDE procedure suggests using at least 5 concentration levels. Based on statistical theory we would expect the number and spacing of concentration levels to affect the outcome, with a larger number of concentrations producing a more reliable estimate. EPA used the Episode 6000 dataset to test this hypothesis.

The IDE procedure suggests spike concentrations at 0.5, 1.0, 2, 4, and 8 times an initial estimate of the IDE (IDE_0). IDE_0 is estimated at 10 times the standard deviation of analytical results of blanks or replicates of the lowest level that can be measured. EPA's Episode 6000 database contain results of analysis of at least 7 replicates at each of at least 16 concentration levels from 0.1 to 100 times the initial estimate of the MDL (a factor of 1000). Between 0.1 and 10 times the MDL, the data are spaced a factor of approximately 1.5 apart. Above 10 times the MDL, the data are spaced at 10, 20, 50 and 100 times the MDL. The reason for the narrow spacing between 0.1 to 10 times the MDL was to attempt to allow more precise characterization of variability in the region of the MDL.

The SL-IDEs and SL-IQEs in Tables 2 and 4, respectively, were computed and reported using all 16 concentration levels because data were available at all of these levels. However, to determine the effect of the IDE procedure, a separate data analysis was performed. In this separate analysis, concentration levels were limited to a total of 5, and the 5 levels were selected to be as consistent as possible with the levels specified in the IDE procedure; i.e., at 5, 10, 20, 40, and 80 times the standard deviation of replicate measurements of a blank or the lowest level at which measurements could be made. The statement "lowest level at which measurements can be made" was interpreted to mean inclusion or

exclusion of results containing zeros and/or negative numbers. For purposes of this evaluation, concentrations that produced results containing a zero or negative number were excluded; i.e., the lowest concentration that contained no zeros or negative numbers was chosen as the concentration at which the standard deviation would be calculated for the purpose of estimating IDE_0 and IQE_0. Zeros and negative numbers were used in all of the other steps in calculating SL-IDEs and SL-IQEs.

The SL-IDE was calculated after selecting the levels based on IDE_0, and the results were compared to results produced when all 16 levels were included in calculating the SL-IDE. Results are summarized in Table 8. This table shows that the median percent difference between the 6-point IDE and the 16-point IDE is approximately -24.9% (where negative percent differences indicate that the 5-point IDE is less than the 16-point IDE). For those instances in which the same model was chosen (108 out of 198), the median percent difference was -35.6%, which was significantly different from 0% based on both the Wilcoxon rank-sum test and the sign test ($p < 0.0001$ for both tests). For those instances in which a different model was chosen (90 out of 198), the median percent difference was 1.3%, which was not significantly different from 0% based on either test (Wilcoxon: $p=0.85$; sign test: $p>0.99$). Because the choice of model can have a confounding effect on any differences between 16-point and 5-point SL-IDEs, the focus should be on the instances in which the same model was chosen. For these instances, the results indicate that only data in the region of detection and quantitation should be used to establish a detection or quantitation limit.

A similar comparison was performed between SL-IQEs (10%) calculated using all concentration levels to SL-IQEs (10%) calculated using only 5 concentration levels. Results of this comparisons are summarized in Table 9. While differences between the two calculations were not significant based on either the sign test ($p=0.567$) or the Wilcoxon test ($p=0.345$), the differences were larger than those between SL-IDEs, as seen by the larger median percent difference of -194.6%. Unlike the IDE comparison, a different model was used to calculate the 5-point SL-IQE than was used to calculate the 16-point SL-IQE for most analytes. For these 145 analytes, the percent differences were large (median percent difference = 613.9%) but not systematically positive or negative (sign test: $p=0.507$, Wilcoxon: $p=0.606$). For the 50 analytes for which the same model was used to calculate the 5-point and 16-point SL-IQEs, the percent differences were strongly negative (median percent difference = -2,442.7%) and significantly less than 0 (sign test: $p=0.015$, Wilcoxon: $p=0.0007$).

The reason for the use of 5 versus 16 concentration levels yielded significantly different results for the SL-IDE, but not for the SL-IQE, was likely due to the different model types that are recommended in the ASTM IDE and IQE procedures. Systematic differences in the calculated limit appear to occur when the same model type is applied to the 5-point and 16-point datasets. Because the exponential model is chosen based on the significance tests for most analytes in the IDE procedure, the model type used rarely differs between the two sets. There was less consistency in selecting models in the IQE procedure, and the choice of model differed between the 5-point and 16-point SL-IQE for approximately 75% of the analytes. Some of these differences, such as using the constant model instead of the hybrid model for the 5-point SL-IQE calculation, appeared to result in higher SL-IQEs, while others, such as using the linear of hybrid model in place of the constant model for the 5-point calculation, appeared to yield lower SL-IQEs. Therefore, while differences in the selected model resulted in large percent differences, these differences were not consistently positive or negative.

Relative Standard Deviation at the ML and SL-IQE in the Episode 6000 Study

The minimum level of quantitation (ML) is directed at the level at which 10% relative standard deviation (RSD) is attained. However, because the ML is not established at exactly 10% RSD, but is determined by multiplying the standard deviation that is obtained in determination of an MDL by 10 (as recommended by both ACS and Currie for ACS and ISO/IUPAC LOQs), the resulting RSD may not be 10%. The Episode 6000 data provided the opportunity to determine the actual value of the RSD at the ML. For analytes that did not have a spike concentration at the ML, the RSD was determined by linear interpolation between spike levels. Results of the determination showed that the overall median RSD at the ML across all analytes in the Episode 6000 study was 9%, and the median RSD for the 10 analytical techniques ranged between 4 and 16 percent. For 29 analytes, no RSD could be calculated because signals were not generated for samples spiked at the ML. This was likely due to limitations with this dataset that are discussed earlier in this Appendix (see "EPA's Variability versus Concentration Studies"). For 114 of the 169 remaining analytes, the RSD fell between 5% and 15%. Among the analytes that fell outside this range, 28 had RSDs below 5% and 27 had RSDs greater than 15%.

Because IQEs target a specified RSD, RSDs were also calculated based on the SL-IQEs calculated for the Episode 6000 data. Unlike the ML, the SL-IQE procedure does not contain a rounding step and, therefore, the calculated value never corresponded to one of the spike levels used in the study. For this reason, interpolation was required to calculate RSDs at the given SL-IQE value. The overall median RSD based on the SL-IQEs was 7%, with method-specific median RSDs ranging from 6% to 11%. No RSD could be calculated for 9 analytes because signals were not generated for samples spiked immediately above or below the SL-IQE. Similarly to the ML, this was likely due to issues with this dataset that are discussed earlier in this Appendix.

Effect of Outliers on Detection/Quantitation Calculations

The detection and quantitation limits based on the Episode 6000 dataset presented in Tables 2 through 5 were calculated without removing any outlying results. This decision was made based on several reasons. There were generally only 7 results per spike level for each analyte, which is a very small dataset for which to apply outlier tests and removal. In addition, MDL and ML procedures do not include outlier removal steps and, therefore, removing outliers for any of the other procedures would hinder comparisons of the calculated limits themselves. However, based on stakeholder comments, an assessment of the effect of outlier removal procedures on the different detection and quantitation limits was added to this Appendix.

Table 11 shows MDLs and SL-IDEs calculated after Grubbs outlier test (Grubbs F.E. "Procedures for Detecting Outlying Observations in Samples," *Technometrics*, vol. 11 No. 1 1969) was applied to the data. Grubbs test was run at the 5% significance level, and a maximum of one result per spike level was removed based on the results of the test. The choice of outlier test and the associated significance level follows instructions in ASTM-D2777. However, a significance level of 1% is more appropriate for outlier removal tests, as a small sample size coupled with the significance level of 5% can lead to inappropriate removal of outliers. This is true especially for studies evaluating multiple concentrations. For example, in the Episode 6000 study, there were 16 concentrations and 149 of the 198 analytes considered had an outlier present at one or more concentrations based on application of Grubbs test with 5% significance level.

For each analyte, the percent difference of the SL-IDE or MDL calculated using all data compared to the SL-IDE or MDL (calculated using the data after outlier removal) was determined. Summary statistics of these ratios are presented in Table 11. Analytes without outliers are not included in the table or the analyses discussed in this section.

Generally, SL-IDEs decreased slightly when outliers were removed. This is not surprising, as the removal of an outlying result decreases the variability at that spike level. The decrease in the SL-IDEs was not large, however, as the median percent difference comparing SL-IDEs calculated with and without outlier removal was 14.3%, where a positive percent difference indicates that the SL-IDE calculated without outlier removal was greater than the SL-IDE calculated after outlier removal. For a few analytes, removing outliers led to a change in the choice of model used to calculate the SL-IDE. In these cases, the presence of the outliers generally forced the constant model to be used; when outliers were removed, the exponential model was used. Therefore, the change in the calculated SL-IDE for these analytes was greater (median percent difference = 114.7%).

Removal of outliers only changed the MDL results if outlier removal changed the choice of spike levels used to calculate the MDL, or occurred at one of the spike levels from which the original MDL was calculated. This occurred for 60 of the 149 analytes for which any outliers were removed. In these cases, the decrease in the MDL was slightly larger than the change in the SL-IDEs (median percent difference = 30.2%).

For a small subset of analytes, either the SL-IDE or MDL increased after outlier removal. Generally, these increases were very small, and were likely due to increased tolerance factors or decreased mean recoveries for the SL-IDE, or to increased t-statistics for the MDL.

SL-IQEs and MLs calculated with and without outlier removal are presented in Table 12. The effect of outlier removal on calculated SL-IQEs and MLs was generally similar to that on the SL-IDEs and MDLs. For the SL-IQE, the choice of model changed more frequently than for the SL-IDE (31 analytes compared to 8 for the SL-IDE). However, the median percent difference was almost equal to that for the SL-IDE (16.3%). The calculated ML changed based on outlier removal for only 31 analytes, compared to 60 for the MDL. This number was smaller than for the MDL because the ML rounding frequently overshadowed the effect of outliers. However, for the ML, the changes that did occur were greater (median percent difference = 66.7%).

Evaluation of IDE/IQE Procedures

Comparison of IDE and IQEs calculated using Different Models

In the February 2003 Assessment Document, EPA expressed concern about the large amount of variability between calculated IDEs and IQEs resulting from the four different model types, and the subjectivity involved in selecting the most appropriate model. One stakeholder commented that this concern was not valid, and that IDEs calculated using different models were generally very close. To test this statement, EPA calculated SL-IDEs and SL-IQEs using each of the four major model types, and calculated RSDs between the different values for each analyte ("cross-model RSDs"). The resulting SL-IDEs are presented in Table 13. Median RSDs calculated for all analytes are presented at the bottom of the table. For several analytes, the calculated SL-IDE based on the linear model was negative due to the negative intercept of the fitted model. Because the ASTM procedure for calculating the IDE states

that the linear model should not be used in these instances, the SL-IDE based on the linear model was not included in these RSD calculations.

There is a large amount of variability between RSDs calculated with these data using the different models. Generally, SL-IDEs calculated using the constant model were much greater than those calculated using the other models. The hybrid model yielded the lowest SL-IDEs, excluding cases where the linear model SL-IDE was negative. The SL-IDEs calculated using the hybrid and exponential models were quite similar for some analytes, but quite different for others. When examined separately by method, the variability between models was generally smaller for metals methods than organics methods. However, there was a large difference in cross-model RSDs between the two metals methods, (i.e., IDEs across models in Method 1620 had a median RSD of 27%, whereas IDEs across models in Method 200.8 had a median RSD of 88%).

RSDs between SL-IQEs calculated using the different models are included in Table 14. The variability between the different model estimates was similar to that of the SL-IDEs, with a median RSD of 136% between SL-IQEs (10%). Method-specific median cross-model RSDs among SL-IQEs (10%) ranged from 24% for Method 1620 to 166% for Method 524.2.

To assess the effect of interlaboratory variability on the differences between estimates calculated from different models, cross-model RSDs were determined between the different IDEs and IQEs calculated based on the interlaboratory validation studies of Methods 1631 and 1638. These RSDs are presented in Table 7. Based on these data, the variability between model estimates appears to increase when the variability between laboratories is included. Cross-model RSDs between the IDEs calculated from the different model types ranged between 61% and 162%, with a median of 123%. These RSDs are greater than those calculated using the single-laboratory metals data in Episode 6000. Variability between IQEs was smaller than the variability between IDEs. Cross-model RSDs between IQEs ranged between 50% and 190%, with a median of 99%.

Comparison of IDE/IQEs Calculated Using Different Software Packages

A stakeholder commenting on EPA's February 2003 data assessment stated that the Agency's concerns about the complexity and subjectivity in the IDE and IQE procedures were unimportant due in part to the availability of software that will automatically perform the IDE and IQE calculations. EPA obtained two software packages from this stakeholder (see the section titled "Computations") to aid in responding to this and other comments regarding the calculation of IDEs and IQEs in the February 2003 TSD.

EPA compared these two software programs using a random subset of 20 analytes from the Episode 6000 dataset. To ensure that differences between results were due to the programs themselves, the same data were used for each program. Table 15 presents a comparison of the IDE and IQE_{10} (IQE at 10% RSD) results based on the two software packages, along with limits calculated using SAS programs (the latter limits match those presented in Tables 2 and 4). In addition, summary statistics of this comparison are presented in Table 16. Comparisons between IDEs and IQEs calculated using QCalc and the Excel software could not be done for all models, because QCalc only performs each calculation using two of the four models (exponential and hybrid for the IDE calculation, and linear and hybrid for the IQE calculation).

Generally, IDEs and IQEs calculated using SAS programs were very close to those determined using QCalc based on the same model type. The median ratio of the IDE or IQE calculated using SAS compared to the IDE or IQE calculated using QCalc equaled 0.99 or 1.00 for all model types. For two analytes (1,1,-dichloroethene and selenium by Method 1620) the hybrid IDEs and IQEs differed greatly between QCalc and the SAS programs. This appeared to be because the intercept term estimated by QCalc was negative for these analytes (resulting in negative IDEs and IQEs), whereas the intercept term estimated by SAS was approximately the positive absolute value of this estimate (resulting in positive IDEs and IQEs).

IDEs and IQEs calculated using the Excel file were generally comparable to those calculated using the SAS programs and QCalc for the constant, linear, and exponential models. The differences between the values calculated using the Excel file and other packages, however, were much greater for the hybrid model. As seen by the median ratios, the estimated IDEs and IQEs determined based on the hybrid model using Excel were slightly higher than those determined using SAS, and approximately twice those determined using QCalc. Part of this difference is due to the negative values calculated by QCalc for two analytes. However, the calculated values differed greatly, as the resulting IQEs calculated by Excel using the hybrid model ranged from less than 0 to more than 6 times greater than that calculated using the SAS programs. These differences seem to be due to how the hybrid model is fit using Excel. The Solver add-in function used by Excel does not seem to follow the same Newton's Non-Linear Least Squares algorithm described in the ASTM procedures and followed by EPA's SAS programs and QCalc.

In addition to differences in calculated limits based on the same model type, the different programs may yield different IDEs or IQEs based on which model type is indicated as most appropriate by a particular software package. QCalc and the Excel file both automatically suggest the same model type for the IDE and IQE. However, EPA often used a different model type for calculating the IDE and IQE. This was done because the ASTM IDE procedure lists constant, linear, and exponential as the three major model types to be considered, whereas the ASTM IQE procedure lists the constant, linear, and hybrid as the three major model types. Therefore, while the exponential model was used by EPA to calculate most IDEs, it was not used to calculate any of the IQEs. Because of this, while EPA and QCalc selected the same model type to calculate the IDE for only one analyte, the same model type was selected to calculate the IQE for 17 of the 20 analytes.

The Excel file frequently chose a different model type than QCalc and the EPA SAS programs to calculate the IDE and IQE. The Excel file selected a different model type than QCalc for 14 of the 20 analytes, and selected a different model than EPA's SAS program to calculate the IDE and IQE for 19 and 17 analytes, respectively. The reason for this appears to be that the Excel file suggests that the appropriate decision be based on which model has the smallest sum of squared residuals. This is different from the statistical tests of slope and curvature used by QCalc and the SAS programs and also described in the ASTM procedures. While both QCalc and the Excel file also include graphs to aid in model selection, and could potentially yield more consistent model selection through these graphs, it is likely that many users would prefer the clearer answer provided by statistical tests or comparisons of sums of squared residuals.

Based on these differences in selecting and fitting models, it does not appear that the two available software programs remove all complexity and subjectivity from the calculation of IDEs and IQEs. Instead, they appear to introduce new issues by using steps not included in the ASTM procedures. While QCalc appears to follow the ASTM procedures more closely than the Excel file, it does not perform

calculations for all model types and, therefore, may introduce greater subjectivity by only providing calculated limits based on inappropriate models.

Effect Of Long-Term Variability

Several stakeholders commenting on EPA's assessment expressed concern about the lack of long-term variability included in the MDL procedure. Commenters state that the lack of long-term variability leads to underestimates of Currie's critical value (L_C). In addition, ACIL included datasets containing results of blank samples analyzed over three months for 5 analytes to show this effect. These commenters pointed to the ACIL procedures for calculating the critical level (CRV) and long-term MDL (ACIL LT-MDL) and the USGS procedure for calculating the long-term MDL (LT-MDL), which include the collection of blanks over a long period of time.

EPA assessed the effect of long-term variability on calculated limits by simulating multiple 7-replicate subsets from the full dataset, and comparing these short-term CRVs to the CRV calculated using the full dataset. Subsets were created by taking each set of 7 consecutive blanks, (i.e., the first 7 blanks analyzed would be one subset, the 2nd through 8th blanks analyzed would be another subset, etc.). This yielded a total of n-6 subsets, where n is the number of total blanks for that analyte. Because a blank will be used in as many as 7 subsets, the variability of the short-term CRVs was lower than what would be expected; however, the approach was used to yield the greatest number of simulated subsets. The CRV was then calculated for each subset:

$$CRV_i = \overline{X}_i + s_i * t_{(0.99,6)}$$

where CRV_i, $\overline{X}_i$, and s_i are the critical value, the mean, and the standard deviation for the i^{th} simulated subset of blank results, respectively. The overall CRV was calculated using the same formula, using the mean and standard deviation based on all blank results and a lower t-statistic based on the greater number of blank replicates. Table 17 shows the results of the comparison of calculated short-term and long-term CRVs for the five analytes.

While the range of days from which sets of 7 replicates were simulated varied from between one week to greater than 3 weeks, graphical analyses did not show any effect of the number of days on the resulting CRV. The total number of blanks also did not seem to have an effect on the percentage of short-term CRVs that exceeded the overall CRV. The mean short-term CRV was generally very close to the overall CRV for each analyte. However, for three of the five analytes, the majority of the short-term CRVs exceeded were lower than the overall CRV, indicating that long-term variability did have an effect on the resulting limit. For the other analytes, the effect of any added variability was counteracted by the smaller t-statistic used in the calculation. These t-statistics ranged between 2.4 and 2.5 between analytes, well below the 3.14 used when only 7 replicates are available.

One possible reason for the number of short-term CRVs falling below the overall CRV was the presence of outliers. The ACIL procedure permits the use of an outlier procedure to remove outlying high or low blanks. EPA used Grubbs test and identified 3 blank results for silver, and 1 blank result each for barium and chromium, as outliers. After removal of these results, the overall and short-term CRVs were re-calculated for these 3 analytes. The results of these calculations are given in Table 18.

Because an outlying result is used in the calculation of the overall CRV (but only for a maximum of 7 of the short-term CRVs), the effect of outlier removal was greater for the overall CRV than on the short-term CRVs. For all 3 analytes, the majority of the short-term CRVs were above the overall CRV, and the mean short-term CRV was slightly higher than the overall CRV. This was consistent with the results of cadmium and copper shown in Table 17, for which no outliers were detected. Because no information was available about why these results could have been outlying, it is not known if they were the result of a known error, or were in fact the result of the long-term variability included in the study. However, it appears that the effect of long-term variability is generally not large when compared to the effect of using more replicates on the t-statistic multiplier.

As stated in Section 3.3.3, a greater number of replicates will yield improved estimates of standard deviation and, therefore, better estimates of Currie's L_C. Based on this, although, EPA does not feel estimations of L_C based on 7 replicates are biased low, these estimates may be less precise than those based on greater replicates. The large variability of the 7-replicate CRVs can be seen in the large ranges of short-term CRVs calculated with and without outlier removal. The use of the higher t-statistic also seems to counteract the added long-term variability. The ACIL procedure suggests 7-replicate CRVs are underestimates, and should therefore be multiplied by a factor of 2. The short-term CRV calculated in the ACIL procedure is based on blanks analyzed in a single batch and, therefore, are not comparable to the short-term CRVs simulated by EPA. However, such a multiplier is not necessary in calculating the MDL, even if long-term variability is not included in the analyses.

SUMMARY

Public comment on the February 2003 Assessment Document and the proposed regulatory revisions expressed many divergent views about the merits and usefulness of EPA's 2003 assessment and proposed regulatory revisions. We recognize that there is a broad interest in improving current procedures and uses, but no consensus for a specific procedure or procedures has emerged among the laboratory, industry, regulatory or regulated communities. Thus, we have withdrawn the March 2003 proposed revisions and, to meet the terms of the settlement agreement that is described in chapter 1, are taking final action on the 2003 Assessment Document in this Revised Assessment Document. This is not the end of our efforts to work together, as stakeholders have suggested, to discuss mutual concerns and possible solutions. We look forward to continued stakeholder participation in an ongoing dialog about the development and use of detection and quantitation limits in CWA programs.

In this appendix, we have compared detection and quantitation limits computed from data gathered by EPA or submitted to EPA. This comparison shows that, in general, detection limits derived from a single concentration level such as EPA's MDL are, on average, approximately the same as detection limits derived from similar approaches such as the ACS LOD and LOQ and ISO/IUPAC CRV and MDV, and are approximately three times lower than a single-laboratory variant of ASTM's IDE; and that all quantitation limit approaches, such as EPA's ML, the ACS and ISO/IUPAC LOQ, and a single-laboratory variant of ASTM's IQE, produce quantitation limits that are generally only slightly different. In addition, the following are general statements about the datasets and/or analyses described in this appendix.

1. *Variability of Results*
Comparisons of detection and quantitation limits show high variability among the limits calculated using the different approaches, even with data containing 7 replicates at 16 concentration levels (see

the summary statistics at the end of Tables 3, 5, and 7). The net effect is that the systematic differences among detection and quantitation limits produced by the various approaches are overwhelmed by variability; i.e., there is a small systematic difference among the approaches but great variability in the detection and quantitation limits for a given analyte. This result is not surprising given the variability of data in the region of detection and quantitation. However, it is difficult to postulate a solution to the problem. Gathering more data in the region of detection and quantitation would appear to be a solution, but 91 data points were gathered for each analyte in the region between 0.1 and 10 times the MDL in the Episode 6000 studies, and it is unlikely that any organization could afford to gather even this amount of data for determination of a detection limit. Given the high degree of variability of the data, EPA's approach of conducting a single-laboratory study to gain a first estimate, followed by multiple single-laboratory studies to verify or revise the estimate, and an interlaboratory study, where warranted, to further verify and revise the estimate, is a reasonable means of establishing detection and quantitation limits because of the checks and balances that occur at each step.

2. *Regression Analysis*

Using a regression line to estimate a recovery correction at zero concentration causes great swings in the resulting detection and quantitation limits such as the ISO/IUPAC MDV and LOQ. The estimated regression parameters for the recovery models were often not significant, and the inclusion of the estimated slope and the standard errors of the slope and intercept will, therefore, unnecessarily bias the calculated MDV and LOQ, such that the calculated MDVs may be negative (see Discussion section "Negative detection limits for the ISO/IUPAC MDV, and Table 2 for instances of negative detection limits"). The estimated recovery model used in calculating the IDE and IQE is also strongly affected by the chosen model of variability vs. concentration (see Tables 13 and 14). Even though a linear regression is used to model recovery in each case, the weights used in the model are calculated based on the variability model, and can vary greatly when the number of concentrations used is low. For the Episode 6000 data, the median RSD of the recovery slopes from the four different models used in the IDE calculations for a given analyte and method was 5%. In addition, for 77 of the analytes and methods (39%), at least one estimated recovery slope was greater than 1, and at least one was less than 1. This suggests that the method could be considered to be high biased (and the final IDE and IQE would be decreased by the recovery correction) and low biased (and the final IDE and IQE increased) for the analyte, depending on the chosen precision model. For many analytes the slopes were not significantly different from 1, suggesting that a recovery correction may not be appropriate at all. This is in addition to the philosophical issue as to whether recovery correction is warranted. If there is to be a correction for recovery, it may be better to use some average or median value than a regression, or use a measured value near the region of interest.

3. *IDE and IQE*

Additional development of the ASTM IDE and IQE is needed before they can be used routinely, not only because of the complexity of the procedures, but also because of the ambiguity in determining that the correct model has been selected. While different software packages are available that perform most of the calculations, there are many inconsistencies between these programs, and between the programs and the ASTM procedures, that add another area of subjectivity to the determination of IDE and IQEs. (For the consequences of model selection, compare the IDEs and IQEs determined by EPA and EPRI in Table 6, and the IDEs and IQEs calculated from the different

model types in Table 7. Some differ considerably as a result of model selection in application of the IDE and IQE procedures by different statisticians. In addition, the use of different software may lead to the selection of different models, as seen in Table 15.)

4. *Quantitation Limit Approaches*
Quantitation limit approaches such as EPA's ML and the ACS and ISO/IUPAC LOQ that are directed 10% RSD actually produce RSDs that are in the range of the 10% intended (see the discussion in the Section titled "RSD at the ML in the Episode 6000 Study"). The median RSDs for each method in the Episode 6000 dataset ranged from 6% to 16%, and 58% of the individual analyte RSDs fell between 5% and 15%.

Commenters on our February 2003 Assessment Document suggested that procedures submitted by a laboratory association (ACIL) and the U.S. Geological Survey as alternatives to the MDL and ML should be considered. We agree, have evaluated these procedures in this Revised Assessment Document, and believe they provide a starting point for continued stakeholder discussions.

Regarding these two procedures, we note the ACIL CRV generally yielded lower false positive rates than the USGS LT-MDL. This likely was due to the nonparametric estimate of variability used in the USGS procedure. False positive rates for the EPA MDL, which uses a parametric variability but does not include the mean blank result, were lower than the USGS LT-MDL, which does include the mean blank result. The ACIL procedure states that calculated CRVs are based on fewer replicates and/or short-term variability are biased low, and includes optional alternate calculations to use in these situations. However, comparison of CRVs calculated with full set of long-term blanks to those calculated with subsets of 7 blanks suggest that the absence of long-term variability is counteracted by the larger t-statistic used when the number of blank results is smaller.

ACIL also included a separate procedure for methods for which analysis of blank samples does not always produce a signal. The idea of dividing methods into two groups has merit. However, the current ACIL procedure for these methods often generates estimates of Currie's L_C that are above the estimate of Currie's L_D when contamination is present.

TABLES

Table 1. Datasets Suggested by Petitioners

Dataset and year	Analyte and technology
AAMA 1996-7	Metals by ICP/AES (200.7)
AAMA 1996-7	Mercury by CVAA (245.2)
AAMA 1996-7	PCBs by GC/ECD (608.2)
MMA 2000-1	PCB 1216 and 1260 by GC/ECD
EPA/EPRI 1997-8	Mercury by CVAF (1631)
EPA/EPRI 1997-8	Metals by ICP/MS (1638)
EPRI 1987	Metals by GFAA (EPA 200)
EPRI 1990	Metals by ICP/AES (EPA 200.7)
EPRI 1994	Ai, Be, Tl by GFAA (EPA 200)
EPRI 1996	Cd, As, Cr by GFAA (EPA 200)

Table 2. Comparison of Detection Limits (µg/L except where footnoted) for the Episode 6000 Dataset

Analyte	Method	Procedure	EPA/ ACS DL	ISO CRV	ISO MDV	ASTM SL-IDE
1,1,1,2-tetrachloroethane	502.2	ELCD	0.041	0.005	0.009	0.034
1,1,1,2-tetrachloroethane	524.2		0.052	0.039	-0.047	0.244
1,1,1-trichloroethane	502.2	ELCD	0.012	0.009	0.017	0.041
1,1,1-trichloroethane	524.2		0.055	0.021	0.003	0.308
1,1,2,2-tce+1,2,3-tcp	502.2	ELCD	0.064	0.047	0.086	0.179
1,1,2,2-tetrachloroethane	524.2		0.132	0.131	0.128	0.436
1,1,2-trichloroethane	502.2	ELCD	0.024	0.004	0.006	0.032
1,1,2-trichloroethane	524.2		0.075	0.043	0.040	0.319
1,1-dichloroethane	502.2	ELCD	0.010	0.007	0.014	0.083
1,1-dichloroethane	524.2		0.033	0.020	0.016	0.229
1,1-dichloroethene	502.2	ELCD	0.038	0.030	0.073	0.234
1,1-dichloroethene	524.2		0.054	0.035	-0.037	0.335
1,1-dichloropropanone	524.2		5.184	3.146	5.635	6.372
1,1-dichloropropene	524.2		0.045	0.012	-0.030	0.287
1,2,3-trichlorobenzene	502.2	ELCD	0.048	0.034	0.065	0.134
1,2,3-trichlorobenzene	502.2	PID	0.057	0.042	0.088	0.115
1,2,3-trichlorobenzene	524.2		0.070	0.040	0.031	0.275
1,2,3-trichloropropane	524.2		7.328	0.046	0.033	1.263
1,2,4-trichlorobenzene	502.2	ELCD	0.022	0.014	0.030	0.088
1,2,4-trichlorobenzene	502.2	PID	0.070	0.038	0.080	0.124
1,2,4-trichlorobenzene	524.2		0.053	0.050	0.052	0.224
1,2,4-trimethylbenzene	502.2	PID	0.095	0.053	0.119	0.125
1,2,4-trimethylbenzene	524.2		0.012	0.009	0.017	0.144
1,2-dibromo-3-chloropropane	524.2		1.457	0.391	0.701	1.749
1,2-dibromoethane	502.2	ELCD	0.096	0.007	0.013	0.164
1,2-dibromoethane	524.2		0.127	0.117	0.170	0.326
1,2-dichlorobenzene	502.2	ELCD	0.035	0.031	0.061	0.065
1,2-dichlorobenzene	502.2	PID	0.033	0.024	0.054	0.148
1,2-dichlorobenzene	524.2		0.030	0.023	-0.016	0.130
1,2-dichloroethane	502.2	ELCD	0.017	0.003	0.005	0.042
1,2-dichloroethane	524.2		0.039	0.024	0.013	0.258

Table 2. Comparison of Detection Limits (µg/L except where footnoted) for the Episode 6000 Dataset

Analyte	Method	Procedure	EPA/ ACS DL	ISO CRV	ISO MDV	ASTM SL-IDE
1,2-dichloropropane	502.2	ELCD	0.023	0.014	0.029	0.043
1,2-dichloropropane	524.2		0.056	0.030	0.026	0.247
1,3,5-tmb+4-chlorotoluene	502.2	PID	0.067	0.045	0.100	0.114
1,3,5-trimethylbenzene	524.2		0.011	0.008	0.008	0.135
1,3-dichlorobenzene	502.2	ELCD	0.035	0.005	0.010	0.118
1,3-dichlorobenzene	502.2	PID	0.093	0.077	0.170	0.126
1,3-dichlorobenzene	524.2		0.023	0.016	-0.014	0.143
1,3-dichloropropane	502.2	ELCD	0.016	0.008	0.015	0.047
1,3-dichloropropane	524.2		0.038	0.024	-0.015	0.202
1,4-dichlorobenzene	502.2	ELCD	0.026	0.005	0.009	0.061
1,4-dichlorobenzene	524.2		0.023	0.017	-0.044	0.140
1-chlorobutane	524.2		0.020	0.016	0.018	0.220
2,2-dichloropropane	524.2		2.376	0.103	-0.159	0.691
2-butanone	524.2		0.417	0.297	0.511	0.833
2-chlorotoluene	502.2	ELCD	0.108	0.029	0.056	0.175
2-chlorotoluene	502.2	PID	0.238	0.135	0.302	0.230
2-chlorotoluene	524.2		0.016	0.009	0.002	0.136
2-hexanone	524.2		1.316	0.148	0.231	0.902
2-nitropropane	524.2		0.901	0.275	0.452	1.082
4-chlorotoluene	502.2	ELCD	0.110	0.027	0.050	0.149
4-chlorotoluene	524.2		0.010	0.008	0.007	0.123
4-isopropyltoluene	524.2		0.010	0.008	0.003	0.117
4-methyl-2-pentanone	524.2		0.812	0.480	0.733	1.195
Acetone	524.2		0.859	0.440	0.804	2.120
Acrylonitrile	524.2		0.863	0.444	0.653	1.333
Allyl Chloride	524.2		0.032	0.026	0.005	0.229
Aluminum	1620		29.555	15.043	28.666	206.975
Aluminum	200.8		19.145	1.690	3.547	12.747
Ammonia as Nitrogen [1]	350.3		0.010	0.007	0.014	0.014
Antimony	1620		1.552	0.801	1.754	4.260
Antimony	200.8		0.178	0.003	0.007	0.019
Arsenic	1620		1.065	0.917	1.375	1.410

Table 2. Comparison of Detection Limits (µg/L except where footnoted) for the Episode 6000 Dataset

Analyte	Method	Procedure	EPA/ ACS DL	ISO CRV	ISO MDV	ASTM SL-IDE
Arsenic	200.8		0.226	0.137	0.272	0.366
Barium	1620		1.702	1.337	1.831	1.837
Barium	200.8		0.033	0.029	0.061	0.084
Benzene	502.2	PID	0.030	0.029	0.067	0.079
Benzene	524.2		0.014	0.014	0.026	0.125
Beryllium	1620		0.528	0.339	0.408	0.448
Beryllium	200.8		0.007	0.004	0.006	0.024
Boron	1620		15.387	10.356	17.792	21.161
Bromobenzene	502.2	ELCD	0.131	0.093	0.186	0.765
Bromobenzene	502.2	PID	0.012	0.009	0.019	0.050
Bromobenzene	524.2		0.044	0.036	-0.060	0.211
Bromochloromethane	502.2	ELCD	0.013	0.012	0.024	0.482
Bromochloromethane	524.2		0.125	0.113	0.159	0.345
Bromodichloromethane	502.2	ELCD	0.004	0.003	0.005	0.075
Bromodichloromethane	524.2		0.043	0.026	0.019	0.205
Bromoform	502.2	ELCD	0.006	0.003	0.001	1.513
Bromoform	524.2		0.123	0.065	0.031	0.400
Bromomethane	502.2	ELCD	0.267	0.219	0.358	7.293
Bromomethane	524.2		0.068	0.055	0.056	0.280
Cadmium	1620		0.127	0.079	0.134	0.191
Cadmium	200.8		0.004	0.007	0.012	0.022
Calcium	1620		36.726	35.822	72.397	41.358
Carbon Disulfide	524.2		0.027	0.015	-0.040	0.239
Carbon Tetrachloride	524.2		0.038	0.027	-0.040	0.314
Carbontet+1,1-dcp	502.2	ELCD	0.029	0.008	0.016	0.072
Chloroacetonitrile	524.2		0.919	0.773	1.527	1.569
Chlorobenzene	502.2	ELCD	0.011	0.010	0.022	0.460
Chlorobenzene	502.2	PID	0.030	0.025	0.055	0.064
Chlorobenzene	524.2		0.025	0.022	0.012	0.133
Chloroethane	502.2	ELCD	0.108	0.008	0.009	2.598
Chloroethane	524.2		0.066	0.041	0.038	0.395
Chloroform	502.2	ELCD	0.043	0.006	0.009	0.032

Table 2. Comparison of Detection Limits (µg/L except where footnoted) for the Episode 6000 Dataset

Analyte	Method	Procedure	EPA/ ACS DL	ISO CRV	ISO MDV	ASTM SL-IDE
Chloroform	524.2		0.036	0.027	0.021	0.225
Chloromethane	502.2	ELCD	0.070	0.049	0.130	0.250
Chloromethane	524.2		0.045	0.036	0.065	0.253
Chromium	1620		0.310	0.254	0.386	0.496
Chromium	200.8		0.073	0.062	0.125	0.408
Cis-1,2-dce+2,2-dcp	502.2	ELCD	0.013	0.009	0.016	0.055
Cis-1,2-dichloroethene	524.2		0.040	0.033	-0.023	0.234
Cis-1,3-dichloropropene	502.2	ELCD	0.007	0.002	0.004	0.074
Cis-1,3-dichloropropene	502.2	PID	0.057	0.048	0.099	0.082
Cis-1,3-dichloropropene	524.2		0.038	0.024	-0.004	0.173
Cobalt	1620		9.820	4.017	8.094	16.463
Cobalt	200.8		0.001	0.001	-0.067	0.074
Copper	1620		6.046	4.990	10.512	21.189
Copper	200.8		0.037	0.027	0.053	0.798
Dibromochloromethane	502.2	ELCD	0.009	0.006	0.011	0.436
Dibromochloromethane	524.2		0.051	0.031	0.004	0.287
Dibromomethane	502.2	ELCD	0.007	0.005	0.010	0.460
Dibromomethane	524.2		0.102	0.082	0.112	0.388
Dichlorodifluoromethane	502.2	ELCD	0.009	0.003	-0.020	0.240
Dichlorodifluoromethane	524.2		0.083	0.054	0.037	0.560
Diethyl Ether	524.2		0.120	0.114	0.163	0.376
Ethyl Methacrylate	524.2		0.045	0.031	0.013	0.273
Ethylbenzene	502.2	PID	0.021	0.015	0.035	0.078
Ethylbenzene	524.2		0.033	0.028	-0.024	0.198
Hardness [1]	130.2		0.828	0.554	1.152	2.258
Hexachlorobutadiene	502.2	ELCD	0.043	0.010	0.021	0.094
Hexachlorobutadiene	524.2		0.068	0.035	-0.031	0.308
Hexachloroethane	524.2		0.056	0.049	0.038	0.288
Hexchlobutadiene+naphthalene	502.2	PID	0.649	0.143	0.321	0.597
Iron	1620		90.409	270.433	472.249	373.590
Isopropylbenzene	502.2	PID	0.020	0.015	0.035	0.060
Isopropylbenzene	524.2		0.011	0.010	0.010	0.120

Table 2. Comparison of Detection Limits (µg/L except where footnoted) for the Episode 6000 Dataset

Analyte	Method	Procedure	EPA/ ACS DL	ISO CRV	ISO MDV	ASTM SL-IDE
Lead	1620		1.647	1.186	1.965	2.423
Lead	200.8		0.655	0.061	0.120	0.204
M+p Xylene	502.2	PID	0.090	0.012	0.026	0.121
M+p Xylene	524.2		0.013	0.008	0.004	0.142
Magnesium	1620		103.033	88.729	175.316	105.998
Manganese	1620		6.856	1.081	2.591	6.808
Manganese	200.8		0.031	0.030	0.049	0.109
Mercury	200.8		0.004	0.003	-0.018	0.027
Methacrylonitrile	524.2		0.356	0.228	0.362	0.718
Methyl Iodide	524.2		0.025	0.023	-0.013	0.193
Methyl Tert-butyl Ether	524.2		0.026	0.016	-0.033	0.225
Methyla crylate	524.2		0.220	0.202	0.353	0.601
Methylene Chloride	502.2	ELCD	0.128	1.835	4.917	2.841
Methylene Chloride	524.2		0.082	0.072	0.093	0.314
Methylm ethacryl ate	524.2		0.225	0.085	0.117	0.535
Molybdenum	1620		2.455	1.714	3.787	3.034
Molybdenum	200.8		0.004	0.003	0.000	0.271
N-butylbenzene	502.2	PID	0.030	0.023	0.049	0.141
N-butylbenzene	524.2		0.016	0.014	0.026	0.152
N-propylbenzene	502.2	PID	0.040	0.022	0.049	0.092
N-propylbenzene	524.2		0.038	0.026	-0.053	0.284
Naphthalene	524.2		0.048	0.040	0.044	0.186
Nickel	1620		20.219	13.262	25.697	25.560
Nickel	200.8		0.146	0.058	0.107	0.083
o-xylene	524.2		0.018	0.015	-0.032	0.198
o-xylene+styrene	502.2	PID	0.059	0.037	0.082	0.116
P-isopropotol+1,4-dcb	502.2	PID	0.073	0.056	0.123	0.159
Pentachloroethane	524.2		0.553	0.019	-0.100	0.408
Sec-butylbenzene	502.2	PID	0.055	0.032	0.075	0.081
Sec-butylbenzene	524.2		0.014	0.011	-0.012	0.140
Selenium	1620		0.849	0.619	1.493	1.975
Selenium	200.8		0.192	0.156	0.302	0.416

Table 2. Comparison of Detection Limits (µg/L except where footnoted) for the Episode 6000 Dataset

Analyte	Method	Procedure	EPA/ ACS DL	ISO CRV	ISO MDV	ASTM SL-IDE
Silver	1620		4.907	3.588	6.495	10.668
Silver	200.8		0.004	0.002	0.004	0.012
Sodium	1620		69.530	49.595	97.649	138.768
Styrene	524.2		0.014	0.011	0.010	0.141
Tert-butybenzene	502.2	PID	0.029	0.020	0.047	0.074
Tert-butybenzene	524.2		0.022	0.012	0.023	0.186
Tetrachloroethene	502.2	ELCD	0.018	0.014	0.029	0.061
Tetrachloroethene	502.2	PID	0.062	0.040	0.094	0.156
Tetrachloroethene	524.2		0.085	0.084	0.047	0.469
Thallium	1620		0.512	0.651	1.406	1.153
Thallium	200.8		0.000	0.000	0.001	0.001
Thorium	200.8		0.001	0.001	-0.005	0.001
Tin	1620		3.670	2.019	3.143	3.932
Titanium	1620		4.777	4.453	8.050	5.376
Toluene	502.2	PID	0.070	0.028	0.063	0.064
Toluene	524.2		0.020	0.006	-0.004	0.146
Total Phosphorus [1]	365.2		0.006	0.005	0.009	0.013
Total Suspended Solids [1]	160.2		1.170	0.948	1.945	3.005
Trans-1,2-dichloroethene	502.2	ELCD	0.041	0.041	0.090	0.081
Trans-1,2-dichloroethene	524.2		0.038	0.032	-0.016	0.300
Trans-1,3-dichloropropene	502.2	ELCD	0.012	0.003	0.005	0.098
Trans-1,3-dichloropropene	502.2	PID	0.058	0.045	0.095	0.092
Trans-1,3-dichloropropene	524.2		0.051	0.025	-0.007	0.223
Trans-1,4-dichloro-2-butene	524.2		0.512	0.348	0.576	1.250
Trichloroethene	502.2	ELCD	0.012	0.001	0.003	0.059
Trichloroethene	502.2	PID	0.027	0.018	0.042	0.097
Trichloroethene	524.2		0.061	0.058	0.056	0.332
Trichlorofluoromethane	502.2	ELCD	0.108	0.249	0.612	2.079
Trichlorofluoromethane	524.2		0.087	0.075	0.038	0.384
Uranium	200.8		0.000	0.000	0.000	0.000
Vanadium	1620		7.344	4.207	8.359	10.630
Vanadium	200.8		0.555	0.512	0.994	0.864

Table 2. Comparison of Detection Limits (µg/L except where footnoted) for the Episode 6000 Dataset

Analyte	Method	Procedure	EPA/ ACS DL	ISO CRV	ISO MDV	ASTM SL-IDE
Vinyl Chloride	502.2	ELCD	0.270	0.039	0.077	3.672
Vinyl Chloride	524.2		0.043	0.031	-0.007	0.365
WAD Cyanide	1677		0.572	0.169	0.319	0.701
Xylene (Total)	524.2		0.009	0.005	0.007	0.128
Yttrium	1620		1.923	1.370	2.518	3.247
Zinc	1620		2.597	2.301	3.697	4.500
Zinc	200.8		0.900	0.461	0.806	1.598

[1] Results reported as mg/L

Note: ELCD or PID in the Procedure column indicates the photo-ionization detector (PID) or electrolytic conductivity detector (ELCD) in EPA Method 502.2

Table 3. Percent Differences of Detection Limits to the EPA/ACS DL for the Episode 6000 Dataset

Analyte	Method	Procedure	ISO CRV/ MDL	ISO MDV/ MDL	SL-IDE/ MDL
1,1,1,2-tetrachloroethane	502.2	ELCD	-159.2%	-131.0%	-20.3%
1,1,1,2-tetrachloroethane	524.2		-28.9%	-4142.5%	129.8%
1,1,1-trichloroethane	502.2	ELCD	-34.4%	32.1%	108.8%
1,1,1-trichloroethane	524.2		-89.4%	-177.7%	139.1%
1,1,2,2-tce+1,2,3-tcp	502.2	ELCD	-29.7%	29.9%	94.7%
1,1,2,2-tetrachloroethane	524.2		-0.6%	-3.4%	107.0%
1,1,2-trichloroethane	502.2	ELCD	-146.2%	-116.9%	27.6%
1,1,2-trichloroethane	524.2		-53.2%	-60.4%	124.0%
1,1-dichloroethane	502.2	ELCD	-40.1%	31.0%	156.8%
1,1-dichloroethane	524.2		-50.5%	-70.3%	150.0%
1,1-dichloroethene	502.2	ELCD	-25.4%	61.8%	143.5%
1,1-dichloroethene	524.2		-42.8%	-1080.2%	144.1%
1,1-dichloropropanone	524.2		-48.9%	8.3%	20.6%
1,1-dichloropropene	524.2		-117.1%	-1021.1%	146.2%
1,2,3-trichlorobenzene	502.2	ELCD	-34.9%	30.2%	94.9%
1,2,3-trichlorobenzene	502.2	PID	-29.4%	42.0%	67.0%
1,2,3-trichlorobenzene	524.2		-53.5%	-76.9%	119.2%
1,2,3-trichloropropane	524.2		-197.5%	-198.2%	-141.2%

Table 3. Percent Differences of Detection Limits to the EPA/ACS DL for the Episode 6000 Dataset

Analyte	Method	Procedure	ISO CRV/ MDL	ISO MDV/ MDL	SL-IDE/ MDL
1,2,4-trichlorobenzene	502.2	ELCD	-39.7%	31.4%	121.2%
1,2,4-trichlorobenzene	502.2	PID	-59.9%	13.5%	55.5%
1,2,4-trichlorobenzene	524.2		-5.0%	-1.3%	123.6%
1,2,4-trimethylbenzene	502.2	PID	-55.5%	23.0%	28.0%
1,2,4-trimethylbenzene	524.2		-25.8%	33.0%	168.6%
1,2-dibromo-3-chloropropane	524.2		-115.4%	-70.1%	18.2%
1,2-dibromoethane	502.2	ELCD	-172.1%	-150.8%	52.9%
1,2-dibromoethane	524.2		-8.6%	28.7%	87.8%
1,2-dichlorobenzene	502.2	ELCD	-12.4%	53.6%	59.5%
1,2-dichlorobenzene	502.2	PID	-30.7%	48.9%	127.6%
1,2-dichlorobenzene	524.2		-28.0%	-655.2%	125.1%
1,2-dichloroethane	502.2	ELCD	-140.1%	-106.3%	83.9%
1,2-dichloroethane	524.2		-48.6%	-98.0%	147.5%
1,2-dichloropropane	502.2	ELCD	-45.0%	22.4%	61.1%
1,2-dichloropropane	524.2		-59.7%	-75.2%	125.7%
1,3,5-tmb+4-chlorotoluene	502.2	PID	-39.6%	39.4%	51.0%
1,3,5-trimethylbenzene	524.2		-33.9%	-28.8%	169.3%
1,3-dichlorobenzene	502.2	ELCD	-151.2%	-112.2%	108.7%
1,3-dichlorobenzene	502.2	PID	-19.1%	58.3%	30.0%
1,3-dichlorobenzene	524.2		-35.5%	-754.8%	144.1%
1,3-dichloropropane	502.2	ELCD	-63.5%	-2.1%	100.1%
1,3-dichloropropane	524.2		-45.7%	-457.8%	136.4%
1,4-dichlorobenzene	502.2	ELCD	-136.9%	-94.1%	80.6%
1,4-dichlorobenzene	524.2		-33.3%	654.4%	142.5%
1-chlorobutane	524.2		-24.0%	-11.7%	166.8%
2,2-dichloropropane	524.2		-183.3%	-228.6%	-109.9%
2-butanone	524.2		-33.5%	20.2%	66.6%
2-chlorotoluene	502.2	ELCD	-116.2%	-64.0%	47.7%
2-chlorotoluene	502.2	PID	-55.5%	23.6%	-3.6%
2-chlorotoluene	524.2		-54.7%	-165.4%	158.1%
2-hexanone	524.2		-159.6%	-140.3%	-37.3%
2-nitropropane	524.2		-106.6%	-66.3%	18.2%

Table 3. Percent Differences of Detection Limits to the EPA/ACS DL for the Episode 6000 Dataset

Analyte	Method	Procedure	ISO CRV/ MDL	ISO MDV/ MDL	SL-IDE/ MDL
4-chlorotoluene	502.2	ELCD	-119.9%	-74.8%	30.5%
4-chlorotoluene	524.2		-21.8%	-26.2%	170.8%
4-isopropyltoluene	524.2		-18.2%	-95.8%	169.2%
4-methyl-2-pentanone	524.2		-51.4%	-10.3%	38.1%
Acetone	524.2		-64.5%	-6.6%	84.7%
Acrylonitrile	524.2		-64.0%	-27.7%	42.9%
Allyl Chloride	524.2		-19.8%	-150.4%	150.6%
Aluminum	1620		-65.1%	-3.1%	150.0%
Aluminum	200.8		-167.6%	-137.5%	-40.1%
Ammonia as Nitrogen	350.3		-39.8%	30.4%	31.7%
Antimony	1620		-63.8%	12.2%	93.2%
Antimony	200.8		-193.1%	-185.9%	-161.5%
Arsenic	1620		-14.9%	25.4%	27.9%
Arsenic	200.8		-49.1%	18.7%	47.5%
Barium	1620		-24.0%	7.3%	7.6%
Barium	200.8		-12.2%	59.9%	87.9%
Benzene	502.2	PID	-2.5%	76.2%	89.5%
Benzene	524.2		-1.9%	57.8%	158.7%
Beryllium	1620		-43.8%	-25.6%	-16.5%
Beryllium	200.8		-55.8%	-16.7%	109.7%
Boron	1620		-39.1%	14.5%	31.6%
Bromobenzene	502.2	ELCD	-33.8%	34.8%	141.6%
Bromobenzene	502.2	PID	-31.6%	44.4%	121.7%
Bromobenzene	524.2		-18.1%	1274.8%	131.5%
Bromochloromethane	502.2	ELCD	-11.8%	55.9%	189.2%
Bromochloromethane	524.2		-10.3%	23.8%	93.6%
Bromodichloromethane	502.2	ELCD	-35.9%	27.1%	178.8%
Bromodichloromethane	524.2		-47.8%	-76.2%	130.5%
Bromoform	502.2	ELCD	-64.7%	-129.0%	198.4%
Bromoform	524.2		-62.6%	-120.5%	105.6%
Bromomethane	502.2	ELCD	-19.7%	29.2%	185.9%
Bromomethane	524.2		-21.0%	-19.6%	122.1%

Table 3. Percent Differences of Detection Limits to the EPA/ACS DL for the Episode 6000 Dataset

Analyte	Method	Procedure	ISO CRV/ MDL	ISO MDV/ MDL	SL-IDE/ MDL
Cadmium	1620		-47.1%	5.5%	40.1%
Cadmium	200.8		55.5%	99.6%	138.8%
Calcium	1620		-2.5%	65.4%	11.9%
Carbon Disulfide	524.2		-52.8%	990.7%	160.0%
Carbon Tetrachloride	524.2		-33.8%	10302.8%	156.6%
Carbontet+1,1-dcp	502.2	ELCD	-110.8%	-55.2%	85.6%
Chloroacetonitrile	524.2		-17.3%	49.7%	52.3%
Chlorobenzene	502.2	ELCD	-11.3%	61.5%	190.3%
Chlorobenzene	502.2	PID	-19.2%	58.8%	71.4%
Chlorobenzene	524.2		-12.7%	-66.3%	137.5%
Chloroethane	502.2	ELCD	-171.0%	-169.4%	184.1%
Chloroethane	524.2		-47.0%	-53.1%	142.6%
Chloroform	502.2	ELCD	-150.5%	-129.4%	-27.3%
Chloroform	524.2		-29.2%	-51.9%	144.5%
Chloromethane	502.2	ELCD	-34.7%	60.2%	112.8%
Chloromethane	524.2		-21.8%	37.1%	139.8%
Chromium	1620		-20.0%	21.9%	46.3%
Chromium	200.8		-16.5%	52.5%	139.3%
Cis-1,2-dce+2,2-dcp	502.2	ELCD	-39.4%	21.8%	124.0%
Cis-1,2-dichloroethane	524.2		-19.1%	-760.6%	141.9%
Cis-1,3-dichloropropene	502.2	ELCD	-101.0%	-61.1%	164.6%
Cis-1,3-dichloropropene	502.2	PID	-17.5%	54.1%	36.0%
Cis-1,3-dichloropropene	524.2		-47.6%	-251.5%	127.2%
Cobalt	1620		-83.9%	-19.3%	50.6%
Cobalt	200.8		-23.4%	206.3%	194.5%
Copper	1620		-19.1%	53.9%	111.2%
Copper	200.8		-33.0%	35.3%	182.2%
Dibromochloromethane	502.2	ELCD	-46.7%	17.2%	191.8%
Dibromochloromethane	524.2		-49.9%	-168.4%	139.6%
Dibromomethane	502.2	ELCD	-21.1%	38.8%	194.4%
Dibromomethane	524.2		-21.5%	9.2%	116.8%
Dichlorodifluoromethane	502.2	ELCD	-91.4%	511.1%	185.7%

Table 3. Percent Differences of Detection Limits to the EPA/ACS DL for the Episode 6000 Dataset

Analyte	Method	Procedure	ISO CRV/ MDL	ISO MDV/ MDL	SL-IDE/ MDL
Dichlorodifluoromethane	524.2		-42.3%	-76.4%	148.1%
Diethyl Ether	524.2		-4.9%	30.4%	103.3%
Ethyl Methacrylate	524.2		-37.9%	-108.3%	143.1%
Ethylbenzene	502.2	PID	-35.2%	46.8%	113.8%
Ethylbenzene	524.2		-18.3%	-1245.1%	142.3%
Hardness	130.2		-39.6%	32.7%	92.6%
Hexachlorobutadiene	502.2	ELCD	-123.8%	-69.6%	74.3%
Hexachlorobutadiene	524.2		-63.3%	-528.0%	127.6%
Hexachloroethane	524.2		-12.4%	-38.6%	134.9%
Hexchlobutadiene+naphthalene	502.2	PID	-127.7%	-67.8%	-8.4 %
Iron	1620		99.8%	135.7%	122.1%
Isopropylbenzene	502.2	PID	-30.2%	53.0%	98.7%
Isopropylbenzene	524.2		-8.3%	-3.3%	167.1%
Lead	1620		-32.6%	17.6%	38.1%
Lead	200.8		-165.8%	-138.0%	-105.1%
M+p Xylene	502.2	PID	-154.5%	-109.6%	28.6%
M+p Xylene	524.2		-51.9%	-100.0%	166.8%
Magnesium	1620		-14.9%	51.9%	2.8 %
Manganese	1620		-145.5%	-90.3%	-0.7%
Manganese	200.8		-2.7%	45.4%	112.6%
Mercury	200.8		-22.3%	331.3%	145.0%
Methacrylonitrile	524.2		-43.7%	1.8%	67.4%
Methyl Iodide	524.2		-7.9%	-613.8%	153.7%
Methyl Tert-butyl Ether	524.2		-45.4%	1591.3%	158.7%
Methylacrylate	524.2		-8.6%	46.5%	92.9%
Methylene Chloride	502.2	ELCD	173.9%	189.8%	182.7%
Methylene Chloride	524.2		-13.4%	12.6%	117.2%
Methylmethacrylate	524.2		-90.7%	-63.2%	81.6%
Molybdenum	1620		-35.5%	42.7%	21.1%
Molybdenum	200.8		-25.1%	-195.0%	194.5%
N-butylbenzene	502.2	PID	-26.9%	49.2%	130.0%
N-butylbenzene	524.2		-11.7%	50.0%	162.5%

Table 3. Percent Differences of Detection Limits to the EPA/ACS DL for the Episode 6000 Dataset

Analyte	Method	Procedure	ISO CRV/ MDL	ISO MDV/ MDL	SL-IDE/ MDL
N-propylbenzene	502.2	PID	-58.0%	20.6%	77.9%
N-propylbenzene	524.2		-38.7%	1215.0%	152.9%
Naphthalene	524.2		-19.7%	-8.6%	117.7%
Nickel	1620		-41.6%	23.9%	23.3%
Nickel	200.8		-86.4%	-30.4%	-55.2%
o-xylene	524.2		-22.0%	735.4%	166.0%
o-xylene+styrene	502.2	PID	-46.2%	32.4%	65.1%
P-isopropotol+1,4-dcb	502.2	PID	-25.1%	51.8%	74.3%
Pentachloroethane	524.2		-186.5%	-288.7%	-30.2%
Sec-butylbenzene	502.2	PID	-52.4%	29.7%	37.9%
Sec-butylbenzene	524.2		-27.1%	2196.0%	163.9%
Selenium	1620		-31.3%	55.0%	79.8%
Selenium	200.8		-20.4%	44.8%	73.8%
Silver	1620		-31.1%	27.9%	74.0%
Silver	200.8		-77.6%	-5.4%	102.6%
Sodium	1620		-33.5%	33.6%	66.5%
Styrene	524.2		-22.6%	-31.1%	163.6%
Tert-butylbenzene	502.2	PID	-36.4%	48.6%	88.6%
Tert-butylbenzene	524.2		-60.7%	5.5%	157.8%
Tetrachloroethene	502.2	ELCD	-26.2%	47.3%	109.0%
Tetrachloroethene	502.2	PID	-42.6%	41.5%	86.4%
Tetrachloroethene	524.2		-0.3%	-57.5%	138.9%
Thallium	1620		24.0%	93.3%	77.0%
Thallium	200.8		-18.1%	44.5%	67.0%
Thorium	200.8		-17.9%	270.2%	50.1%
Tin	1620		-58.1%	-15.5%	6.9%
Titanium	1620		-7.0%	51.0%	11.8%
Toluene	502.2	PID	-85.5%	-11.0%	-8.1%
Toluene	524.2		-112.6%	-290.2%	152.2%
Total Phosphorus	365.2		-25.1%	44.5%	77.5%
Total Suspended Solids	160.2		-21.0%	49.7%	87.9%
Trans-1,2-dichloroethene	502.2	ELCD	1.2%	75.2%	66.8%

Table 3. Percent Differences of Detection Limits to the EPA/ACS DL for the Episode 6000 Dataset

Analyte	Method	Procedure	ISO CRV/ MDL	ISO MDV/ MDL	SL-IDE/ MDL
Trans-1,2-dichloroethene	524.2		-18.1%	-495.6%	154.9%
Trans-1,3-dichloropropene	502.2	ELCD	-117.4%	-79.8%	157.3%
Trans-1,3-dichloropropene	502.2	PID	-26.6%	47.3%	44.8%
Trans-1,3-dichloropropene	524.2		-69.2%	-260.7%	125.8%
Trans-1,4-dichloro-2-butene	524.2		-38.0%	11.8%	83.8%
Trichloroethene	502.2	ELCD	-156.0%	-127.8%	133.2%
Trichloroethene	502.2	PID	-38.3%	42.8%	112.7%
Trichloroethene	524.2		-4.9%	-9.7%	137.6%
Trichlorofluoromethane	502.2	ELCD	78.9%	140.1%	180.3%
Trichlorofluoromethane	524.2		-15.3%	-78.4%	125.9%
Uranium	200.8		-75.4%	-32.9%	27.6%
Vanadium	1620		-54.3%	12.9%	36.6%
Vanadium	200.8		-8.0%	56.7%	43.6%
Vinyl Chloride	502.2	ELCD	-149.6%	-111.4%	172.7%
Vinyl Chloride	524.2		-32.6%	-274.6%	157.7%
WAD Cyanide	1677		-108.6%	-56.8%	20.2%
Xylene (Total)	524.2		-54.0%	-20.8%	174.0%
Yttrium	1620		-33.6%	26.8%	51.2%
Zinc	1620		-12.1%	34.9%	53.6%
Zinc	200.8		-64.6%	-11.0%	55.8%

Note: ELCD or PID in the Procedure column indicates the photo-ionization detector (PID) or electrolytic conductivity detector (ELCD) in EPA Method 502.2

Summary Statistics for Table 3

	ISO CRV/ EPA/ACS DL % Difference	ISO MDV/ EPA/ACS DL % Difference	SL-IDE/ EPA/ACS DL % Difference
Minimum	-197.5%	-4142.5%	-161.5%
25th percentile	-60.5%	-76.4%	51.0%
Median	-35.7%	8.8%	108.7%
75th percentile	-19.9%	44.5%	144.1%
Maximum	173.9%	10302.8%	198.4%
	Median % Difference	p-value for % difference=0	
CRV vs. DL	-35.7%	<0.0001	
MDV vs. DL	8.8%	0.164	
SL-IDE vs. DL	1087%	<0.0001	

Table 4. Comparison Quantitation Limits for the Episode 6000 Dataset (µg/L except where footnoted)

Analyte	Method	Procedure	EPA/ ACS QL	ISO/ IUPAC LOQ	ASTM SL-IQE
1,1,1,2-tetrachloroethane	502.2	ELCD	0.2	0.023	0.030
1,1,1,2-tetrachloroethane	524.2		0.2	0.183	0.181
1,1,1-trichloroethane	502.2	ELCD	0.05	0.044	0.830
1,1,1-trichloroethane	524.2		0.2	0.102	0.240
1,1,2,2-tce+1,2,3-tcp	502.2	ELCD	0.2	0.227	5.514
1,1,2,2-tetrachloroethane	524.2		0.5	0.597	0.569
1,1,2-trichloroethane	502.2	ELCD	0.1	0.018	0.060
1,1,2-trichloroethane	524.2		0.2	0.212	0.290
1,1-dichloroethane	502.2	ELCD	0.05	0.037	0.527
1,1-dichloroethane	524.2		0.1	0.099	0.115
1,1-dichloroethene	502.2	ELCD	0.1	0.191	3.796
1,1-dichloroethene	524.2		0.2	0.159	0.129
1,1-dichloropropanone	524.2		20	15.409	12.705
1,1-dichloropropene	524.2		0.2	0.057	0.180
1,2,3-trichlorobenzene	502.2	ELCD	0.2	0.168	0.851
1,2,3-trichlorobenzene	502.2	PID	0.2	0.226	0.248

Table 4. Comparison Quantitation Limits for the Episode 6000 Dataset (µg/L except where footnoted)

Analyte	Method	Procedure	EPA/ ACS QL	ISO/ IUPAC LOQ	ASTM SL-IQE
1,2,3-trichlorobenzene	524.2		0.2	0.192	0.216
1,2,3-trichloropropane	524.2		20	0.268	11.316
1,2,4-trichlorobenzene	502.2	ELCD	0.1	0.078	0.401
1,2,4-trichlorobenzene	502.2	PID	0.2	0.208	0.439
1,2,4-trichlorobenzene	524.2		0.2	0.231	0.141
1,2,4-trimethylbenzene	502.2	PID	0.5	0.307	0.653
1,2,4-trimethylbenzene	524.2		0.05	0.050	20.896
1,2-dibromo-3-chloropropane	524.2		5	1.842	71.182[6]
1,2-dibromoethane	502.2	ELCD	0.5	0.037	0.592
1,2-dibromoethane	524.2		0.5	0.560	0.417
1,2-dichlorobenzene	502.2	ELCD	0.1	0.158	0.183
1,2-dichlorobenzene	502.2	PID	0.1	0.139	0.346
1,2-dichlorobenzene	524.2		0.1	0.101	0.085
1,2-dichloroethane	502.2	ELCD	0.05	0.015	0.065
1,2-dichloroethane	524.2		0.1	0.122	0.222
1,2-dichloropropane	502.2	ELCD	0.1	0.075	0.102
1,2-dichloropropane	524.2		0.2	0.148	0.196
1,3,5-tmb+4-chlorotoluene	502.2	PID	0.2	0.259	0.189
1,3,5-trimethylbenzene	524.2		0.05	0.044	23.744
1,3-dichlorobenzene	502.2	ELCD	0.1	0.027	0.936
1,3-dichlorobenzene	502.2	PID	0.2	0.438	0.465
1,3-dichlorobenzene	524.2		0.1	0.080	0.076
1,3-dichloropropane	502.2	ELCD	0.05	0.040	0.054
1,3-dichloropropane	524.2		0.1	0.114	0.139
1,4-dichlorobenzene	502.2	ELCD	0.1	0.025	0.101
1,4-dichlorobenzene	524.2		0.1	0.069	0.078
1-chlorobutane	524.2		0.05	0.082	29.943
2,2-dichloropropane	524.2		10	0.572	38.009
2-butanone	524.2		2	1.416	0.893
2-chlorotoluene	502.2	ELCD	0.5	0.145	0.493
2-chlorotoluene	502.2	PID	1	0.781	0.849
2-chlorotoluene	524.2		0.05	0.046	0.053

Table 4. Comparison Quantitation Limits for the Episode 6000 Dataset (µg/L except where footnoted)

Analyte	Method	Procedure	EPA/ ACS QL	ISO/ IUPAC LOQ	ASTM SL-IQE
2-hexanone	524.2		5	0.669	0.442
2-nitropropane	524.2		2	1.280	0.590
4-chlorotoluene	502.2	ELCD	0.5	0.132	0.142 [1]
4-chlorotoluene	524.2		0.05	0.037	23.810
4-isopropyltoluene	524.2		0.05	0.043	0.016
4-methyl-2-pentanone	524.2		2	2.066	1.785
Acetone	524.2		2	2.114	2.741
Acrylonitrile	524.2		2	1.816	28.056
Allyl Chloride	524.2		0.1	0.129	29.674
Aluminum	1620		100	76.242	464.069
Aluminum	200.8		50	9.418	29.684
Ammonia as Nitrogen [2]	350.3		0.05	0.037	0.035
Antimony	1620		5	4.784	9.551
Antimony	200.8		0.5	0.017	0.034
Arsenic	1620		5	3.684	3.097
Arsenic	200.8		1	0.720	0.798
Barium	1620		5	4.722	4.118
Barium	200.8		0.1	0.161	0.211
Benzene	502.2	PID	0.1	0.173	0.182
Benzene	524.2		0.05	0.075	0.044
Beryllium	1620		2	1.055	0.980
Beryllium	200.8		0.02	0.018	0.044
Boron	1620		50	46.040	51.134
Bromobenzene	502.2	ELCD	0.5	0.599	3.529
Bromobenzene	502.2	PID	0.05	0.050	0.100
Bromobenzene	524.2		0.2	0.167	0.140
Bromochloromethane	502.2	ELCD	0.05	0.065	1.598
Bromochloromethane	524.2		0.5	0.549	0.368
Bromodichloromethane	502.2	ELCD	0.02	0.015	0.424
Bromodichloromethane	524.2		0.2	0.135	0.128
Bromoform	502.2	ELCD	0.02	0.018	3.393
Bromoform	524.2		0.5	0.287	0.482

Table 4. Comparison Quantitation Limits for the Episode 6000 Dataset (µg/L except where footnoted)

Analyte	Method	Procedure	EPA/ ACS QL	ISO/ IUPAC LOQ	ASTM SL-IQE
Bromomethane	502.2	ELCD	1	undefined [3]	16.351
Bromomethane	524.2		0.2	0.252	0.226
Cadmium	1620		0.5	0.346	0.410
Cadmium	200.8		0.02	0.046	0.063
Calcium	1620		100	186.530	99.975
Carbon Disulfide	524.2		0.1	0.077	0.101
Carbon Tetrachloride	524.2		0.1	0.127	0.140
Carbontet+1,1-dcp	502.2	ELCD	0.1	0.046	0.069
Chloroacetonitrile	524.2		2	4.170	3.310
Chlorobenzene	502.2	ELCD	0.05	0.058	1.766
Chlorobenzene	502.2	PID	0.1	0.143	0.119
Chlorobenzene	524.2		0.1	0.108	0.059
Chloroethane	502.2	ELCD	0.5	0.053	5.826
Chloroethane	524.2		0.2	0.185	0.255
Chloroform	502.2	ELCD	0.2	0.029	0.025
Chloroform	524.2		0.1	0.138	0.121
Chloromethane	502.2	ELCD	0.2	0.342	1.734
Chloromethane	524.2		0.2	0.181	0.141
Chromium	1620		1	0.993	1.259
Chromium	200.8		0.2	0.331	1.028
Cis-1,2-dce+2,2-dcp	502.2	ELCD	0.05	0.045	0.039
Cis-1,2-dichloroethene	524.2		0.1	0.154	0.144
Cis-1,3-dichloropropene	502.2	ELCD	0.02	0.013	0.415
Cis-1,3-dichloropropene	502.2	PID	0.2	0.254	0.017 [1]
Cis-1,3-dichloropropene	524.2		0.1	0.117	0.141
Cobalt	1620		50	20.916	40.837
Cobalt	200.8		0.005	undefined [3]	undefined [4]
Copper	1620		20	27.513	47.509
Copper	200.8		0.1	0.142	1.825
Dibromochloromethane	502.2	ELCD	0.02	0.030	1.252
Dibromochloromethane	524.2		0.2	0.149	0.288
Dibromomethane	502.2	ELCD	0.02	0.028	1.395

Table 4. Comparison Quantitation Limits for the Episode 6000 Dataset (µg/L except where footnoted)

Analyte	Method	Procedure	EPA/ ACS QL	ISO/ IUPAC LOQ	ASTM SL-IQE
Dibromomethane	524.2		0.5	0.400	0.460
Dichlorodifluoromethane	502.2	ELCD	0.02	0.012	1.091 [5]
Dichlorodifluoromethane	524.2		0.2	0.290	0.480
Diethyl Ether	524.2		0.5	0.563	0.404
Ethyl Methacrylate	524.2		0.2	0.139	0.183
Ethylbenzene	502.2	PID	0.1	0.089	0.157
Ethylbenzene	524.2		0.1	0.123	0.077
Hardness [2]	130.2		2	2.973	5.465
Hexachlorobutadiene	502.2	ELCD	0.2	0.054	0.243
Hexachlorobutadiene	524.2		0.2	0.160	0.228
Hexachloroethane	524.2		0.2	0.232	0.167
Hexchlobutadiene+naphthalene	502.2	PID	2	0.834	1.542
Iron	1620		200	1490.589	996.565 [5]
Isopropylbenzene	502.2	PID	0.1	0.090	0.129
Isopropylbenzene	524.2		0.05	0.056	25.592
Lead	1620		5	5.062	5.698
Lead	200.8		2	0.318	0.685
M+p Xylene	502.2	PID	0.2	0.068	0.222
M+p Xylene	524.2		0.05	0.042	24.651
Magnesium	1620		500	454.043	267.199
Manganese	1620		20	7.948	15.264
Manganese	200.8		0.1	0.133	0.245
Mercury	200.8		0.02	0.056	0.039
Methacrylonitrile	524.2		1	1.066	19.062
Methyl Iodide	524.2		0.1	0.108	0.083
Methyl Tert-butyl Ether	524.2		0.1	0.073	0.122
Methylacrylate	524.2		1	0.966	0.727
Methylene Chloride	502.2	ELCD	0.5	undefined [3]	6.033
Methylene Chloride	524.2		0.2	0.354	0.433
Methylmethacrylate	524.2		1	0.381	20.773
Molybdenum	1620		10	9.752	7.597
Molybdenum	200.8		0.01	0.052	0.608

Table 4. Comparison Quantitation Limits for the Episode 6000 Dataset (µg/L except where footnoted)

Analyte	Method	Procedure	EPA/ ACS QL	ISO/ IUPAC LOQ	ASTM SL-IQE
N-butylbenzene	502.2	PID	0.1	0.128	0.745
N-butylbenzene	524.2		0.05	0.077	0.067
N-propylbenzene	502.2	PID	0.2	0.128	0.186
N-propylbenzene	524.2		0.1	0.110	29.878
Naphthalene	524.2		0.2	0.184	0.108
Nickel	1620		100	66.486	67.206
Nickel	200.8		0.5	0.287	0.183
o-xylene	524.2		0.05	0.062	0.040
o-xylene+styrene	502.2	PID	0.2	0.210	0.181
P-isoproptol+1,4-dcb	502.2	PID	0.2	0.318	0.456
Pentachloroethane	524.2		2	0.086	0.551
Sec-butylbenzene	502.2	PID	0.2	0.193	0.157
Sec-butylbenzene	524.2		0.05	0.063	0.047
Selenium	1620		2	3.859	5.235
Selenium	200.8		0.5	0.805	1.045
Silver	1620		20	16.734	25.842
Silver	200.8		0.02	0.011	0.056
Sodium	1620		200	251.546	337.755
Styrene	524.2		0.05	0.054	0.041
Tert-butylbenzene	502.2	PID	0.1	0.121	0.203
Tert-butylbenzene	524.2		0.1	0.063	0.073
Tetrachloroethene	502.2	ELCD	0.05	0.076	0.122
Tetrachloroethene	502.2	PID	0.2	0.244	0.750
Tetrachloroethene	524.2		0.2	0.378	30.554[6]
Thallium	1620		2	3.748	2.799
Thallium	200.8		0.002	0.002	0.002
Thorium	200.8		0.002	0.005	0.004
Tin	1620		10	9.237	9.406
Titanium	1620		20	20.807	14.236
Toluene	502.2	PID	0.2	0.162	0.194
Toluene	524.2		0.05	0.028	0.046
Total Phosphorus[2]	365.2		0.02	0.024	0.030

Table 4. Comparison Quantitation Limits for the Episode 6000 Dataset (µg/L except where footnoted)

Analyte	Method	Procedure	EPA/ ACS QL	ISO/ IUPAC LOQ	ASTM SL-IQE
Total Suspended Solids [2]	160.2		5	5.011	6.729
Trans-1,2-dichloroethene	502.2	ELCD	0.2	0.234	0.191
Trans-1,2-dichloroethene	524.2		0.1	0.141	0.153
Trans-1,3-dichloropropene	502.2	ELCD	0.05	0.016	0.729
Trans-1,3-dichloropropene	502.2	PID	0.2	0.244	0.175
Trans-1,3-dichloropropene	524.2		0.2	0.121	0.218
Trans-1,4-dichloro-2-butene	524.2		2	1.803	30.108
Trichloroethene	502.2	ELCD	0.05	0.008	3.169
Trichloroethene	502.2	PID	0.1	0.108	0.401
Trichloroethene	524.2		0.2	0.284	0.167
Trichlorofluoromethane	502.2	ELCD	0.5	1.612	4.662
Trichlorofluoromethane	524.2		0.2	0.279	42.490 [6]
Uranium	200.8		0.001	0.001	0.001
Vanadium	1620		20	21.586	24.338
Vanadium	200.8		2	2.627	1.933
Vinyl Chloride	502.2	ELCD	1	0.264	8.234
Vinyl Chloride	524.2		0.2	0.139	0.219
WAD Cyanide	1677		2	0.852	1.624
Xylene (Total)	524.2		0.02	0.027	23.520
Yttrium	1620		5	6.571	8.962
Zinc	1620		10	9.575	10.452
Zinc	200.8		2	2.147	7.024

[1] IQE 10% undefined, IQE 20% reported

[2] Results reported as mg/L

[3] No LOQ could be calculated due to a square root of a negative number in the formula

[4] IQE 10%, IQE 20% and IQE 30% all negative based on chosen model (linear)

[5] IQE 10% and IQE 20% both negative, IQE 30% reported

[6] Hybrid model selected but did not converge; IQE 10% based on constant model instead

Note: ELCD or PID in the Procedure column indicates the photo-ionization detector (PID) or electrolytic conductivity detector (ELCD) in EPA Method 502.2

Table 5. Percent Differences of Quantitation Limits to the EPA/ACS QL for the Episode 6000 Dataset

Analyte	Method	Procedure	ISO LOQ/ML	SL-IQE/ML
1,1,1,2-tetrachloroethane	502.2	ELCD	-158.7%	-147.3%
1,1,1,2-tetrachloroethane	524.2		-8.7%	-9.8%
1,1,1-trichloroethane	502.2	ELCD	-11.8%	177.3%
1,1,1-trichloroethane	524.2		-65.1%	18.0%
1,1,2,2-tce+1,2,3-tcp	502.2	ELCD	12.8%	186.0%
1,1,2,2-tetrachloroethane	524.2		17.6%	12.9%
1,1,2-trichloroethane	502.2	ELCD	-138.2%	-49.6%
1,1,2-trichloroethane	524.2		5.9%	36.6%
1,1-dichloroethane	502.2	ELCD	-28.6%	165.3%
1,1-dichloroethane	524.2		-0.7%	13.7%
1,1-dichloroethene	502.2	ELCD	62.5%	189.7%
1,1-dichloroethene	524.2		-22.8%	-43.3%
1,1-dichloropropanone	524.2		-25.9%	-44.6%
1,1-dichloropropene	524.2		-111.1%	-10.5%
1,2,3-trichlorobenzene	502.2	ELCD	-17.6%	123.9%
1,2,3-trichlorobenzene	502.2	PID	12.2%	21.3%
1,2,3-trichlorobenzene	524.2		-4.2%	7.7%
1,2,3-trichloropropane	524.2		-194.7%	-55.5%
1,2,4-trichlorobenzene	502.2	ELCD	-25.2%	120.2%
1,2,4-trichlorobenzene	502.2	PID	3.8%	74.9%
1,2,4-trichlorobenzene	524.2		14.5%	-34.9%
1,2,4-trimethylbenzene	502.2	PID	-47.8%	26.5%
1,2,4-trimethylbenzene	524.2		0.5%	199.0%
1,2-dibromo-3-chloropropane	524.2		-92.3%	173.7%
1,2-dibromoethane	502.2	ELCD	-172.7%	16.9%
1,2-dibromoethane	524.2		11.3%	-18.1%
1,2-dichlorobenzene	502.2	ELCD	45.1%	58.8%
1,2-dichlorobenzene	502.2	PID	32.9%	110.2%
1,2-dichlorobenzene	524.2		0.6%	-16.5%
1,2-dichloroethane	502.2	ELCD	-108.1%	26.0%
1,2-dichloroethane	524.2		19.7%	75.6%
1,2-dichloropropane	502.2	ELCD	-28.5%	2.3%

Table 5. Percent Differences of Quantitation Limits to the EPA/ACS QL for the Episode 6000 Dataset

Analyte	Method	Procedure	ISO LOQ/ML	SL-IQE/ML
1,2-dichloropropane	524.2		-29.8%	-1.9%
1,3,5-tmb+4-chlorotoluene	502.2	PID	25.7%	-5.5%
1,3,5-trimethylbenzene	524.2		-13.6%	199.2%
1,3-dichlorobenzene	502.2	ELCD	-114.2%	161.4%
1,3-dichlorobenzene	502.2	PID	74.5%	79.7%
1,3-dichlorobenzene	524.2		-22.2%	-27.3%
1,3-dichloropropane	502.2	ELCD	-22.9%	7.5%
1,3-dichloropropane	524.2		13.0%	32.7%
1,4-dichlorobenzene	502.2	ELCD	-120.8%	1.0%
1,4-dichlorobenzene	524.2		-37.2%	-24.2%
1-chlorobutane	524.2		48.8%	199.3%
2,2-dichloropropane	524.2		-178.4%	116.7%
2-butanone	524.2		-34.2%	-76.6%
2-chlorotoluene	502.2	ELCD	-109.9%	-1.4%
2-chlorotoluene	502.2	PID	-24.6%	-16.4%
2-chlorotoluene	524.2		-7.6%	6.3%
2-hexanone	524.2		-152.8%	-167.5%
2-nitropropane	524.2		-43.9%	-108.9%
4-chlorotoluene	502.2	ELCD	-116.3%	-111.5%
4-chlorotoluene	524.2		-29.1%	199.2%
4-isopropyltoluene	524.2		-15.4%	-101.7%
4-methyl-2-pentanone	524.2		3.2%	-11.3%
Acetone	524.2		5.5%	31.3%
Acrylonitrile	524.2		-9.7%	173.4%
Allyl chloride	524.2		25.5%	198.7%
Aluminum	1620		-27.0%	129.1%
Aluminum	200.8	ICP/MS	-136.6%	-51.0%
Ammonia as nitrogen	350.3		-30.9%	-34.1%
Antimony	1620		-4.4%	62.6%
Antimony	200.8	ICP/MS	-186.6%	-174.7%
Arsenic	1620		-30.3%	-47.0%
Arsenic	200.8	ICP/MS	-32.5%	-22.5%