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Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring

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Chapter 1

Introduction

Numerous organizations, such as state pollution control agencies, health departments, local government agencies, industrial dischargers, research facilities, and federal agencies (e.g., EPA, USGS), collect data on effluent and ambient metal concentrations for use in a variety of applications, including: determining attainment status for water quality standards, discerning trends in water quality, estimating effluent concentrations and variability, estimating background loads for total maximum daily loads (TMDLs), assessing permit compliance, and conducting research[1]. The quality of data used is an important issue, and, in particular, the quality of trace level metals data may be compromised due to contamination during sampling, filtration, storage, and analysis. In fact, one of the greatest obstacles faced by laboratories attempting trace metals determinations is the potential for contamination of samples during the sampling and analytical processes. Trace metals are ubiquitous in the environment, and samples can readily become contaminated by numerous sources, including: metallic or metal-containing labware, metal-containing reagents, or metallic sampling equipment; improperly cleaned and stored equipment; and atmospheric inputs such as dirt, dust, or other particulates from exhaust or corroded structures.

The measurement of trace metals at EPA water quality criteria (WQC) levels has been spurred by increased emphasis on a water quality-based approach to the control of toxic pollutants. Current ambient WQC levels[2] for trace metals require measurement capabilities at levels as much as 280 times lower than those levels required to support technology-based controls or achievable by routine analyses in environmental laboratories. Also, recent USGS and EPA studies strongly indicate that rigorous steps must be taken in order to preclude contamination during the collection and analysis of samples for trace metals.

In order to ensure that the data collected for trace metals determinations at ambient water quality criteria levels are valid and not a result of contamination, rigorous quality control (QC) must be applied to all sample collection, preparation, and analysis activities. EPA has published analytical methods (1983, 1991) for monitoring metals in waters and wastewaters, but these methods are inadequate for the determination of ambient concentrations of metals in ambient waters due to the lack of some or all of the essential quality control and handling criteria. This prompted the Engineering and Analysis Division (EAD) to develop new sampling and analytical methods that include the rigorous sample handling and quality control procedures necessary to deliver verifiable data at WQC levels. The new sampling method is entitled, *Method 1669: Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels* ("Method 1669"). The new analytical methods include Methods 1631, 1632, 1636, 1637, 1638, 1639, and 1640 ("the 1600 Series Analysis Methods"). Many of these analysis methods were developed by supplementing existing EPA methods with additional quality control and sample handling requirements; others are new methods that are based on newly developed analytical procedures.

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1 Prothro, M., Acting Assistant Administrator for Water, Memorandum to Water Management Division Directors and Environmental Services Division Directors, Oct. 1, 1993.

2 "Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants; States' Compliance" (also referred to as "The National Toxics Rule"), 40 *CFR* Part 131, (57 *FR* 60848, December 22, 1992).

Appropriate quality assurance (QA) and quality control (QC) procedures are the key to producing precise and accurate data unbiased by contamination. Examination of trace metals data without data from blanks and other QC analyses yields little or no information on whether sample data are reliable. Data quality must be documented through the use of blanks (both field and laboratory blanks), standards, matrix spike/matrix spike duplicates, and field duplicates, as well as other QC analyses. The results of all QC procedures must be included in the data reporting package along with the sample results if data quality is to be known.

The remainder of this document contains guidance that is intended to aid in the review of trace metals data submitted for compliance monitoring purposes under the National Pollutant Discharge Elimination System (NPDES) when these data are collected in accordance with Method 1669 and analyzed by the 1600 Series Analysis Methods. Chapter 2 of this document outlines the data elements that must be reported by laboratories and permittees so that EPA reviewers can validate the data. Chapter 3 provides guidance concerning the review of data collected and reported in accordance with Chapter 2. Chapter 4 provides a *Data Inspection Checklist* that can be used to standardize procedures for documenting the findings of each data inspection.

The guidance provided in these chapters is similar in principle to the data reporting and review guidance provided in EPA's *Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring* (EPA 821-B-93-001), but has been specifically adapted to reflect particular concerns related to the evaluation of data for trace metals.

This guidance is applicable to the examination of recently gathered trace metals data and to historical data in existing EPA databases. It should be noted, however that some qualification of historical data may be required before these data can be included in current databases. A draft *User's Guide to the Quality Assurance/Quality Control Evaluation Scale of Historical Datasets* (12/20/90, available from EPA EMSL-LV), provides guidance that may be used to qualify data for inclusion into current databases. This EMSL-LV guidance stipulates that at least some form of QA/QC must be associated with the historical data for evaluation. This QA/QC may be in the form of various types of blanks (method, field, etc.), replicates field, analytical, etc.), spikes (matrix, surrogate internal standard, etc.), and PE samples (certified reference materials, QC check samples etc.). A scoring mechanism is applied to these QA/QC data, and the usability of the sample data is based on the resulting score.

Chapter 2

Checklist of Laboratory Data Required to Support Compliance Monitoring for Trace Metals Determined in Accordance with Method 1669 and the 1600 Series Analysis Methods

The items listed below describe the minimum data elements necessary to validate trace metals data collected using the *Method for Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels* (Method 1669) and the 1600 Series Analysis Methods. It should be noted that since different instrumentation yields different data output, the specific form of the data will vary according to the analytical method.

1. Method Number

The method number of the EPA analytical method used in conjunction with Method 1669 must be provided. This information will allow a data reviewer and user to become familiar with the method, if necessary, prior to reviewing the data. It will also assist the reviewer and user in making any necessary determinations of the comparability of these data with previously reported data, including qualified historical data. If more than one method is needed to cover a complement of analytes, then all method numbers must be provided. A clear delineation of the specific method used for each given analyte is required. Also, the revision date or revision level and number/letter of the method must be given, so that the reviewer or user tests the results submitted against the specific method used. Table 1 provides a list of EPA methods for analysis of trace metals along with the corresponding water quality criterion published by EPA for each metal or metal species.

In recognition of advances that are occurring in analytical technology, the 1600 Series Analysis Methods are performance-based. That is, an alternate procedure or technique may be used if the performance requirements in the reference method(s) are met. The analyst must start with one of the methods as a reference, and may improve upon this reference method to reduce interferences or lower costs of measurements. Examples include using alternate chelating or ion exchange resins, alternate matrix modifiers, additional cleanup techniques, or more sensitive detectors. The objective of allowing method modifications is to improve method performance on the sample being analyzed. At no time are changes that degrade method performance allowed. Each method details the tests and documentation that are required to support equivalent performance.

2. Detailed Narrative

A detailed narrative discussing any problems with the analysis, corrective actions taken, and changes made to the reference method must be included in a complete data reporting package. Reasons for changes to the reference method, supporting logic behind the technical approach to the change, and the result of the change must be included in the narrative. The narrative should be written by an analytical chemist in terms that another analytical chemist can understand. The results of the review must

be written so that the data user can understand the reason(s) for acceptance/rejection of the data or any changes to the reference method.

3. Data Reporting Forms

The complete data reporting package must include data reporting forms that list all samples analyzed, the metals and metal species determined, and the concentrations found. Analytes detected in *field samples* at concentrations below the minimum level (ML) must be reported as non-detect. However, all analyte concentrations detected in *blank samples* must be reported, regardless of the level. Results must be listed for each sample analyzed, including any dilutions and reanalyses. Metals should be listed by name and CAS Registry number.

The ML is the quantitation level as defined by the EPA 1600 series method used for sample analysis. The laboratory is required to determine the MDL for each analyte in accordance with the procedures described in 40 *CFR* Part 136, Appendix B- *Definition and Procedure for Determination of Method Detection Limit - Revision 1.11*. That MDL multiplied by 3.18 must be less than or equal to the ML given in the EPA 1600 Series Analysis Method.

The use of data qualifiers or flags by the laboratory is discouraged. Rather, laboratories should attempt to correct all analytical problems and provide a detailed narrative that thoroughly describes those problems and the corrective actions taken (see item 2 above). Flags or data qualifiers should be assigned by data users to reflect their specific data quality objectives and uses of the data. If the laboratory submits data with internally generated flags, the laboratory must provide an explanation of the meaning of the flags used.

4. Summary of Quality Control Results

Results for all quality control analyses required by the reference EPA method must be presented in the complete data reporting package. If more than one method was used or if more than one set of samples was analyzed, it must be clearly evident which QC corresponds to a given method and set of samples.

Results for QC procedures that must be provided include, but are not limited to, the following (where applicable):

- Instrument tuning
- Calibration
- Calibration verification (initial and following every 10 analytical samples)
- Initial precision and recovery
- Ongoing precision and recovery
- Blanks
  - Laboratory (method) blanks

- Field blanks
- Calibration blanks
- Equipment blanks

- Matrix spike/matrix spike duplicates
- Field duplicates
- Method of standard additions (MSA) results
- Spectral interference checks
- Serial dilutions
- Internal standard recoveries
- Method detection limits
- Quality control charts and limits

Table 2 lists the required frequency and purpose of the QC procedures.

5. Raw Data

Raw data for all analyses must be kept on file at the laboratory (Chapter 2, Section 7) and submitted for inspection to the data reviewer upon request. The instrument output (emission intensity, peak height, area, or other signal intensity) must be traceable from the raw data to the final result reported. The raw data must be provided for not only the analysis of each field sample but also for all calibrations, verifications, blanks, matrix spike/matrix spike duplicates, field duplicates, and other QC analyses required by the reference method.

Raw data are method and instrument specific and may include, but are not limited to, the following:

- Sample numbers and other identifiers
- Digestion/preparation or extraction dates
- Analysis dates and times
- Analysis sequence/run chronology
- Sample weight or volume
- Volume prior to each extraction/concentration step
- Volume after each extraction/concentration step
- Final volume prior to analysis
- Injection volume
- Matrix modifiers
- Dilution data, differentiating between dilution of a sample or an extract
- Instrument (make, model, revision, modifications)
- Sample introduction system (ultrasonic nebulizer, hydride generator, flow injection system, etc.)
- Column (manufacturer, length, diameter, chelating or ion exchange resin, etc.)
- Operating conditions (char/ashing temperatures, temperature program, incident rf power, flow rates, plasma viewing height, etc.)
- Detector (type, wavelength, slit, analytical mass monitored, etc.)
- Background correction scheme

- Quantitation reports, data system outputs, and other data to link the raw data to the results reported
- Direct instrument readouts (e.g., strip charts, mass spectra, printer tapes, and other recordings of raw data) and other data to support the final results
- Lab bench sheets and copies of all pertinent logbook pages for all field and QC sample preparation and cleanup steps, and for all other parts of the determinations

6. Example Calculations

Example calculations that will allow an independent reviewer to determine how the laboratory used the raw data to arrive at a final result must be provided in the data reporting package if any adjustments are made to the equations included in the methods. Useful examples include both detected and undetected compounds. If the laboratory or the method employs a standardized reporting level for undetected compounds, this should be made clear in the example calculation. Adjustments made for sample volume, dilution, internal standardization, etc. should be evident.

7. Archiving Data on Magnetic Media

It is not necessary for the laboratory or responsible organization to submit digitized binary, hexadecimal, or other raw signal recordings with the data package. However, the laboratory that performs the analysis should archive these data so that the raw reduced data can be reconstructed, and the laboratory or organization responsible for reporting the data should be prepared to submit raw data on magnetic media, upon request by EPA. Magnetic media may be required for automated data review, for diagnosis of data reduction problems, or for establishment of an analytical database.

8. Names, Titles, Addresses, and Telephone Numbers of Analysts and QC Officer

The names, titles, addresses, and telephone numbers of the analysts who performed the determinations and the quality control officer who verified the results must be included in the data reporting package. If the data package is being submitted by a person or organization other than the analytical laboratory, it is that person or organization's responsibility to ensure that the laboratory provides all the data listed above and that all method requirements are met. For example, with regards to effluent or ambient monitoring data submitted by an NPDES permittee on a Discharge Monitoring Report (DMR), the task of collecting and reporting quality control data falls to the permittee.

In addition, the personnel, titles, addresses, telephone numbers, and name (if different from the laboratory that analyzed the field samples) of the facility that cleaned and shipped the sampling equipment and generated the equipment blanks, the laboratory (if different) that analyzed the equipment blanks, and the facility responsible for the collection, filtration, and transport of the field samples to the laboratory must be obtained and included in the data reporting package.

Table 1
Method Numbers, Analytical Techniques, Method Detection Limits, and Minimum Levels

Method	Technique	Metal	MDL (μg/L)[1]	ML (μg/L)[2]	Lowest EPA Water Quality Criterion (ug/L)[3]
1631	Oxidation/Purge & Trap/CVAFS	Mercury	0.00005[4]	0.0002	0.012
1632	Hydride AA	Arsenic	0.002	0.005	0.018
1636	Ion Chromatography	Hexavalent Chromium	0.23	0.5	10.5
1637	CC/STGFAA	Cadmium	0.0074	0.02	0.32
		Lead	0.036	0.1	0.14
1638	ICP/MS	Antimony	0.0097	0.02	14
		Cadmium	0.013	0.1	0.32
		Copper	0.087	0.2	2.5
		Lead	0.015	0.05	0.14
		Nickel	0.33	1	7.1
		Selenium	1.2	5	5
		Silver	0.029	0.1	0.31
		Thallium	0.0079	0.02	1.7
		Zinc	0.14	0.5	28
1639	STGFAA	Antimony	1.9	5	14
		Cadmium	0.023	0.05	0.32
		Trivalent Chromium	0.10	0.2	57
		Nickel	0.65	2	7.1
		Selenium	0.83	2	5
		Zinc	0.14	0.5	28
1640	CC/ICP/MS	Cadmium	0.0024	0.01	0.32
		Copper	0.024	0.1	2.5
		Lead	0.0081	0.02	0.14
		Nickel	0.029	0.1	7.1

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1 Method Detection Limit as determined by 40 *CFR* Part 136, Appendix B

2 Minimum Level (ML) calculated by multiplying laboratory-determined MDL by 3.18 and rounding result to nearest multiple of 1, 2, 5, 10, 20, 50 etc., in accordance with procedures utilized by EAD and described in the EPA *Draft National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection/Quantitation Levels*, March 22, 1994.

3 Lowest of the freshwater, marine, and human health WQC promulgated by EPA for 14 states at 40 *CFR* Part 131 (57 *FR* 60848), with hardness-dependent freshwater aquatic life criteria adjusted in accordance with 57 *FR* 60848 to reflect the worst case hardness of 25 mg/L $CaCO_3$ and all aquatic life criteria adjusted in accordance with the 10/1/93 Office of Water guidance to reflect dissolved metals criteria. A complete listing of all WQC, including total, dissolved, and levels calculated with a hardness of 25 mg/L $CaCO_3$ is provided in Appendix A.

4 MDL for Hg by Method 1631 is an estimated value based on the standard deviation of blank measurements rather than the procedure defined in 40 *CFR* Part 136, Appendix B.

Table 2 -- Quality Control Requirements, Frequency, and Purpose

Required QC Test	Frequency	Purpose
Instrument tuning	Prior to calibration	To assure that the instrument will produce results equivalent to instruments in other laboratories
Calibration (CAL)	Prior to sample analysis and whenever calibration cannot be verified	To establish the working range of the analytical instrument
Calibration verification (VER)	Immediately prior to and following the analysis of every batch of 10 or fewer analytical samples analyzed at the same time	To verify the average response or curve from the initial calibration
Initial precision and recovery (IPR)	Prior to using the method for the first time and each time a modification to the method is made	To establish the ability of the laboratory to generate acceptable precision and recovery
Method detection limit (MDL) and minimum level (ML)	Prior to using the method and whenever there is change that will affect the MDL and ML	To determine the lowest level at which the analyte can be detected with 99% confidence that the concentration is greater than zero
Ongoing precision and recovery (OPR)	Each sample batch (Sample batch size is method specific. Where not specified, batch size is 10.)	To assure that the laboratory remains in control
Blanks	Equipment blank--Prior to use of any sampling equipment at a given site	To assure that contamination of sampling devices and apparatus for sample collection will be detected prior to shipment to the field site
	Calibration blank--Immediately following each calibration verification	To assure that contamination of the analytical system will be detected, if present
	Laboratory (method) blank (BLK)--One method blank per sample batch	To assure that contamination of the analytical process will be detected, if present
	Field blank (FBK)--Every ten samples collected at a given site or at least one per sample site, whichever is more frequent	To assure that contamination of field samples will be detected, if present
Matrix spike/matrix spike duplicate (MS/MSD)	Each batch of 10 or fewer samples from the same site	To determine bias caused by sample matrix effects
Field duplicate	Each batch of 10 or fewer samples from the same site	To measure the precision associated with sample collection, preservation, transportation, and storage procedures, as well as with analytical procedures
Method of standard addition (MSA)	As needed to assure the reliability of results for GFAA or ICP analyses	To compensate for a sample constituent that enhances or depresses the analyte signal
Internal standardization	All analyses by ICP/MS (EPA Methods 200.8 and 200.10)	To correct instrument drift and other variations in the analytical process
Spectral interference check	Prior to using the method for the first time and periodically thereafter as indicated by instrument stability, type of samples analyzed, and expected interferences encountered	To establish corrections for known interelement spectral interferences
Serial dilutions	When analyte concentration is sufficiently high (minimally a factor of 10X the MDL after dilution)	To determine if a chemical or physical interference effect is present

Chapter 3

Guidance for Reviewing Data from the Analysis of Trace Metals Using Method 1669 and the 1600 Series Analysis Methods

Use of the guidelines provided below, or of similarly developed standardized protocols, is highly recommended as a tool with which Regional and State permitting authorities can standardize data inspection and acceptance procedures and minimize differences that might otherwise result between data reviewers and/or permittees responsible for submitting data. A *Data Inspection Checklist* has also been developed and is provided in the following chapter. This checklist provides a standardized format for documenting the findings of each data inspection and an additional tool for standardizing the data review process within a regulatory agency.

1. Purity and Traceability of Reference Standards

The accuracy of any non-absolute empirical measurement is dependent on the reference for that measurement. In determining pollutants in water or other sample matrices, the analytical instrument and analytical process must be calibrated with a known reference material of documented purity and traceability. This information need not be provided with every sample analysis. Rather, it should be maintained on file at the laboratory and provided upon request. When analyses are conducted in a contract laboratory, such documentation should be provided to the permittee the first time that the laboratory is employed for specific analyses and updated as needed.

2. Number of Calibration Points

The 1600 Series Analysis Methods specify that a minimum of three concentrations are to be used when calibrating the instrument. One of these points must be the Minimum Level (ML, see item 5), and another must be near the upper end of the calibration range. Calibration must be performed for each target metal before any samples or blanks are analyzed. The use of the ML as a point on the calibration curve is the principal means by which to assure that measurements made at this quantitation level are reliable.

The data reviewer should review the points used by the laboratory to calibrate the instrument and make certain that the calibration range encompasses the Minimum Level and that all sample and QC measurements are within the calibration range. Samples that produced results which exceeded the calibration range should have been diluted and reanalyzed in accordance with the specifications detailed in the 1600 Series Analysis Method that was used by the laboratory. The diluted sample results need only apply to those analytes that exceeded the calibration range of the instrument. In other words, it is acceptable to use data for different analytes from different levels within the same sample. Some flexibility may be exercised in acceptance of data that are only slightly above ($<10\%$) the calibration range. Such data are generally acceptable as calculated.

If data from an analysis of the diluted sample are not provided, limited use can be made of the data that are above the calibration range ($>10\%$). The response of the analytical instrument to

concentrations of analytes will eventually level off at concentrations above the calibration range. While it is not possible to specify the concentration at which this will occur, it is generally safe to assume that the reported concentration above the calibrated range is a lower limit of the actual concentration. Therefore, if the concentration above the calibration range is also above a regulatory limit, it is a virtual certainty that the actual concentration would also be above that limit.

3. Linearity of Calibration

The relationship between the response of an analytical instrument to the concentration or amount of an analyte introduced into the instrument is referred to as the "calibration curve". An analytical instrument can be said to be calibrated in any instance in which an instrumental response can be related to the concentration of an analyte. The response factor (RF, calculated for external standard calibration) or relative response factor (RRF, calculated for internal standard calibration) is the ratio of the response of the instrument to the concentration of the analyte introduced into the instrument. Equations for calculating RFs and RRFs are provided in the 1600 Series Analysis Methods.

While the shape of calibration curves can be modeled by quadratic equations or higher order mathematical functions, most analytical methods focus on a calibration range in which the linear calibration is essentially a function of the concentration of the analyte. The advantage of the linear calibration is that the RF or RRF represents the slope of calibration curve, simplifying calculations and data interpretation. The 1600 Series Analysis Methods contain specific criteria for determining the linearity of calibration curves determined by either an internal or external standard technique. When the applicable criterion is met, the calibration curve is sufficiently linear to permit the laboratory to use an average RF or RRF, and it is assumed that the calibration curve is a straight line that passes through the zero/zero calibration point. Linearity is determined by calculating the relative standard deviation (RSD) of the RF or RRF for each analyte and comparing this RSD to the specified limit. The specific acceptance criteria are listed in the Data Inspection Checklist (Chapter 4, Item 12) and in the 1600 Series Analysis Methods. These methods also include alternative procedures to be used in the event the linearity criteria fail specifications.

The laboratory must provide the RSD results by which an independent reviewer can judge linearity, even in instances in which the laboratory is using a calibration curve. In these instances, the data reviewer should review each calibration point to assure that the response increases as the concentration increases. If it does not, the instrument is not operating properly, and the data should not be considered valid.

4. Calibration Verification

Calibration verification involves the analysis of a single standard, typically in the middle of the calibration range, at the beginning (and, in some cases, at the end) of each analytical shift. The concentration of each analyte in a reference standard is determined using the initial calibration data and compared to specifications in the method. If results are within the specifications, the laboratory may proceed with analysis without recalibrating. The initial calibration data are then used to quantify sample

results. Specific criteria for acceptance of calibration verifications are provided in the Data Inspection Checklist (Chapter 4, Item 17) and the 1600 Series Analysis Methods.

Calibration verification, which is used in the 1600 Series Analysis Methods, differs in concept and practice from "continuing calibration", which is used in the SW-846 methods and in the Superfund Contract Laboratory Program (CLP). In continuing calibration, a standard is analyzed and new response factors are calculated on the basis of that analysis. If the new factors are close to the average from the initial calibration, all subsequent sample analyses are conducted using the new response factors. The degree of "closeness" is generally measured as the percent difference between the old and new factors. The problem with continuing calibration is that it amounts to a daily single-point calibration. Information about the behavior of the instrument at concentrations above and below this single standard can only be inferred from the initial multiple-point calibration.

The 1600 Series Analysis Methods require calibration verification after every ten samples. Calibration verification is performed by analyzing an aliquot of the mid-point calibration standard, and obtaining results that meet the specifications contained in the methods. These specifications are given for each method and metal as a percentage of the recovery of the mid-point calibration standard. If any individual value falls outside the range given, system performance is considered unacceptable, and the laboratory may either recalibrate the instrument or prepare a new calibration standard and make a second attempt to verify calibration. The data reviewer should verify that each batch of 10 samples is associated with a calibration verification that meets the required performance criteria.

5. Method Detection Limit and Minimum Level

The Minimum Level (ML) is defined in the 1600 Series Analysis Methods as the lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point. Therefore, each 1600 Series Analysis Method requires that the calibration line or curve for each analyte encompass the method-specified ML.

The 1600 Series Analysis Methods also require each laboratory to perform a method detection limit (MDL) study for each analyte in accordance with the procedures given in 40 *CFR* Part 136, Appendix B. The MDL studies are conducted to demonstrate that the laboratory can achieve the MDLs listed in the methods. MDL determinations must be made the first time that the laboratory utilizes the method and each time the laboratory utilizes a new instrument or modifies the method in any way.

Each MDL and ML listed in the 1600 Series Analysis Methods represents the results of MDL studies conducted by the EPA's Engineering and Analysis Division as part of its effort to validate the methods. The MDL studies were conducted by at least one laboratory for each method and metal in accordance with the procedure given in 40 *CFR* Part 136, Appendix B. The MLs shown in Table 1 were calculated by multiplying each laboratory-determined MDL by 3.18 and rounding the result to the nearest multiple of 1, 2, 5, 10, 20, 50, etc. in accordance with the procedures described in the EPA *Draft National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection/Quantitation Levels*, March 22, 1994.

The 1600 Series Analysis Methods and Chapter 2 of this document require the laboratory to report the concentration of all sample results that are at or above the ML. It should be noted that this ML is a sample-specific ML and, therefore, reflects any sample dilutions that were performed. If sample results are reported below the ML, the data reviewer should require the responsible party to correct and resubmit the data, or if this course of action is not possible, the reviewer should determine the sample-specific ML and consider results below that level to be non-detects for regulatory purposes.

If sample results are reported above the ML, but are below the facility's regulatory compliance level, then the data reviewer should consider the results to suggest that the pollutant has been detected but is compliant with the facility's permit (assuming that all QC criteria are met). If sample results are reported above the regulatory compliance level, the data reviewer must evaluate laboratory QC samples in order to verify that the level of pollutant is not attributable to analytical bias. In addition, the data reviewer must evaluate all blank sample results in order to determine if the level of pollutant detected may be attributable to contamination.

Although sample results are to be reported only if they exceed the ML, all blank results are to be reported, regardless of the level. This reporting requirement allows data reviewers the opportunity to assess the impact of any blank contamination on sample results that are reported above the ML.

It is important to remember that if a change that will affect the MDL is made to a method, the MDL procedure must be repeated using the modified procedure. Changes may include alternate digestion, concentration, and cleanup procedures, and changes in instrumentation. Alternate determinative techniques, such as the substitution of a colorimetric technique or changes that degrade method performance are not allowed. The data reviewer should verify that method modifications were appropriate and were capable of producing the desired MDLs.

The procedures given in this document are for evaluation of results for determination of regulatory compliance, and not for assessment of trends, for triggering, or for other purposes. For such other purposes, the reporting of all results, whether negative, zero, below the MDL, above the MDL but below the ML, or above the ML, may be of value and may be required by the permitting authority as necessary to enforce in a particular circumstance. Dealing with the multiplicity of consequences presented by such results, either singly or in combination, is beyond the present scope of this document.

6. Initial Precision and Recovery

The laboratory is required to demonstrate its ability to generate acceptable precision and accuracy data using the techniques specified in the 1600 Series Analysis Methods. This test, which is sometimes termed the "start-up test", must be performed by the laboratory prior to the analysis of field samples with the specified methods and prior to the use of modified versions of the methods on field samples. EPA's experience has been that laboratories that have difficulty passing the start-up test have such marginal performance that they will have difficulty in the routine practice of the method.

The test consists of spiking four aliquots of reagent water with the metals of interest at 2 - 3 times the ML concentrations listed in the methods and analyzing these four aliquots. The mean concentration

(x) and the standard deviation (s) are then calculated for each analyte and compared to the specifications in the methods. If the mean and the standard deviation are within the limits, the laboratory can use the method to analyze field samples.

If the start-up test data fail to meet the specifications in the method, none of the data produced by the laboratory can be considered to be valid. If the laboratory did not perform the start-up tests, the data cannot be valid, unless all other QC criteria have been met and the laboratory has submitted IPR (and associated instrument QC) data that were generated after-the-fact by the same analyst on the same instrument. If these conditions are met, then the data reviewer may consider the data to be acceptable for most purposes. NOTE: The inclusion of this alternative should not in any way be construed to sanction the practice of performing IPR analyses after the analysis of field samples. Rather, EPA believes that demonstration of laboratory capability prior to sample analysis is an essential QC component; this alternative is provided only as a tool to permitting authorities when data have already been collected without the required IPR samples. Once the problem has been identified, all responsible parties are expected to implement corrective action necessary to ensure that it is not repeated.

It is important to remember that if a change is made to a method, the IPR procedure must be repeated using the modified procedure. If the start-up test is not repeated when these steps are modified or added, any data produced by the modified methods cannot be considered to be valid.

7. Analysis of Blanks

Because trace metals are ubiquitous in the environment, the precautions necessary to preclude contamination are more extensive than those required to preclude contamination when synthetic organic compounds and other non-ubiquitous substances are determined. EPA has found that the greatest potential for contamination of samples analyzed for trace metals has been from atmospheric input in the field and laboratory and from inadequate cleaning of sample bottles and labware. In order to prove that such contamination is avoided during sampling, sample transit, and analysis, Method 1669 and the 1600 Series Analysis Methods specify the collection and analysis of numerous blank samples. These include:

- Equipment blanks that are collected prior to the use of any sampling equipment at a given site and provide a means for detecting contamination of sampling devices and apparatus prior to shipment to the field site,

- Field blanks that are collected for each batch of 10 or fewer samples from the same site and provide a means of detecting contamination that arises in the field,

- Calibration blanks that are analyzed immediately after each calibration verification and provide a means of detecting contamination that arises from the analytical system, and

- Laboratory (method) blanks that are analyzed for each batch of samples analyzed on a particular instrument and provide a means of detecting contamination from the analytical process.

While the analysis of a minimum of four blank samples per site may seem to be excessive, particularly when very few (e.g., < 5) samples are collected, EPA has found that the validity of entire studies may be suspect when pollutants are identified in samples that are not associated with each of these blanks. In general, it is not necessary for a facility to report the results of equipment blank analyses unless contamination is identified in field blanks. Therefore, the permittee should obtain equipment blank results from its cleaning facility, maintain these results on file, and provide them to the permitting authority upon request. The data reviewer should evaluate equipment blank results only if it is necessary to identify potential sources of contamination present in field blanks.

Controlling laboratory contamination is an important aspect of the quality assurance plan for the equipment-cleaning facility, laboratory, and field team. Each party should maintain records regarding blank contamination. Typically, these records take the form of a paper trail for each piece of equipment and control charts, and they should be used to prompt corrective action by the party associated with the contamination. For example, if records at a single site suggest that equipment blanks, laboratory blanks, and calibration blanks are consistently clean but that field blanks show consistent levels of contamination, then the field sampling team should re-evaluate their sample handling procedures, identify the problem, and institute corrective actions before collecting additional samples. Similarly, equipment cleaning facilities and laboratories should utilize the results of blank analyses to identify and correct problems in their processes.

Unfortunately, it is often too late for corrective action if data are received that suggest the presence of uncontrolled contamination that adversely affects the associated data. The exception to this rule is the case in which the field and equipment blanks show no discernable levels of contamination, contamination is detected in the laboratory or calibration blanks, sample holding times have not expired, and sufficient sample volume remains to allow the laboratory to identify and eliminate the source of contamination and reanalyze the associated sample(s). In all other cases, the reviewer must exercise one of several options listed below when making use of the data.

- If a contaminant is present in a blank but is not present in a sample, then there is little need for concern about the sample result. (It may be useful, however, to occasionally review the raw data for samples without the contaminant to ensure that the laboratory did not edit the results for this compound.)

- If the sample contains the contaminant at levels of at least 10 times that in the blank, then the likely contribution to the sample from the contaminant in the sample is at most 10%. Since most of the methods in question are no more accurate than that level, the possible contamination is negligible, and the data can be considered to be of acceptable quality.

- If the sample contains the contaminant at levels of at least 5 times but less than 10 times the blank result, the numerical result in the sample should be considered an upper limit of the true concentration, and data users should be cautioned when using such data for enforcement purposes.

- If the sample contains the contaminant at levels below 5 times the level in the blank, the sample data are suspect unless there are sufficient data from analyses of multiple blanks to perform a statistical analysis proving the significance of the analytical result. Such statistical analyses are beyond the scope of this guidance.

- If blank contamination is found in some types of QC samples but not others (e.g., only in the laboratory blank but not in the field blank), the data user should apply the guidelines listed above, but may also use this information to identify the source of contamination and take corrective actions to prevent future recurrences.

There are two difficulties in evaluating sample results relative to blank contamination. First, the reviewer must be able to associate the samples with the correct blanks. Field blanks are associated with each group of field samples collected from the same site. Calibration blanks are associated with samples by the date and time of analysis on a specific instrument. Laboratory (method) blanks are associated with each batch of 10 samples prepared and digested in accordance with a particular method during a single shift. If the reviewer cannot associate a batch of samples with a given blank, the reviewer should request this association from the laboratory so that the results for the samples can be validated.

The second difficulty involves samples that have been diluted. The dilution of the sample with reagent water represents an additional potential source of contamination that will not be reflected in the results for the blank unless the blank was similarly diluted. Therefore, in applying the 10-times rule stated above, the concentration of the sample is compared to the blank results multiplied by the dilution factor of the sample. For instance, if 1.2 ppb of a contaminant is found in the blank, and the associated sample was diluted by a factor of six relative to the extract from the blank prior to analysis, then the diluted sample result would have to be greater than 1.2 x 6 x 10 or 72 ppb to be acceptable. Diluted sample results between 36 and 72 ppb would be considered an upper limit of the actual concentration, and diluted sample results that were less than 36 ppb would be considered unacceptable in the absence of sufficient blank data to statistically prove the significance of the result.

In most cases, the practice of subtracting the concentration reported in the blank from the concentration in the sample is not recommended as a tool to evaluate sample results associated with blank data. One of the most common problems with this approach is that blank concentrations are sometimes higher than one or more associated sample results, yielding negative results.

Nearly all of the 1600 Series Analysis Methods are capable of producing MDLs that are at least 10 times lower than the lowest water quality criteria (WQC) published in the National Toxics Rule. Since most discharge permits require monitoring at levels that are comparable to or higher than the WQC published in the National Toxics Rule, EPA believes that, in nearly all cases, laboratories should be capable of producing blank data that are at least 10 times less than the regulatory compliance level. It should also be noted that laboratories cannot be held accountable for contamination that is present in field blanks but not present in laboratory blanks; in such cases the sampling crew should take corrective measures to eliminate the source of contamination during their sample collection and handling steps.

8. Ongoing Precision and Recovery

The 1600 Series Analysis Methods require laboratories to prepare and analyze an "ongoing precision and recovery" (OPR) sample with each batch of up to 10 samples started through the extraction process on the same twelve hour shift. This OPR sample is identical to the aliquots used in the IPR analyses (see Item 6), and the results of the OPR are used to ensure that laboratory performance is in control during the analysis of the associated batch of field samples.

The data reviewer must verify that the OPR sample has been run with each sample batch and that the applicable recovery criteria in the analytical method have been met. If the recovery criteria have not been met, the reviewer may use the following guidelines when making use of the data:

- If the concentration of the OPR is above method specifications but that analyte is not detected in an associated sample, then it unlikely that the sample result is affected by the failure in the OPR.

- If the concentration of the OPR is above method specifications and that analyte is detected in the sample, then the numerical sample result may represent an upper limit of the true concentration, and data users should be cautioned when using the data for enforcement purposes.

- If the concentration of the OPR is below method specification but that analyte is detected in an associated sample, then the sample result may represent the lower limit of the true concentration for that analyte.

- If the concentration of the OPR is below method specification and that analyte is not detected in an associated sample, then the sample data are suspect and cannot be considered valid for regulatory compliance purposes.

If the OPR standard has not been run, there is no way to verify that the laboratory processes were in control. In such cases, a data reviewer may be able to utilize the field sample data by examining the matrix spike recovery results (see item 9), the IPR results, OPR results from previous and subsequent batches, and any available historical data from both the laboratory and the sample site. If the matrix spike results associated with the sample batch do not meet the performance criteria in the methods, then the results for that set of samples cannot be considered valid. If the laboratory's IPR results and the matrix spike results associated with the sample batch in question meet the all applicable performance criteria in the methods, then the data reviewer may be reasonably confident that laboratory performance was in control during field sample analysis. This level of confidence may be further increased if there is a strong history of both laboratory performance with the method and method performance with the sample matrix in question, as indicated by additional OPR and matrix spike data collected from the laboratory and samples from the same site.

9. Precision and Recovery of Matrix Spike and Matrix Spike Duplicate Compounds

The 1600 Series Analysis Methods require that laboratories spike the analytes of interest into duplicate aliquots of at least one sample from each group of ten samples collected from a single site. The

first of these spiked sample aliquots is known as the matrix spike sample; the second is known as the matrix spike duplicate. These spiked sample aliquots are used to determine if the method is applicable to the sample matrix in question. The 1600 Series Analysis Methods are applicable to the determination of metals at concentrations typically found in ambient water samples and certain treated effluents (e.g., the part-per-trillion to low part-per-billion range). These methods may not be applicable to marine samples and many effluent and in-process samples collected from industrial dischargers. Therefore, it is important to evaluate method performance in the sample matrix of interest.

In evaluating matrix spike sample results, it is important to examine both the precision and accuracy of the duplicate analyses. Precision is assessed by examining the relative percent difference (RPD) of the concentrations found in the matrix spike and matrix spike duplicate samples, and comparing the RPD to the acceptance criteria specified in the analytical method. If the RPD of a matrix spike/matrix spike duplicate pair exceeds the applicable criterion, then the method cannot be considered to be applicable to the sample matrix, and none of the associated sample data can be accepted for regulatory compliance purposes.

If RPD criteria are met, the method is considered to be capable of producing precise data in these samples, and the data reviewer must then verify that the method is capable of producing accurate data. Accuracy is assessed by examining the recovery of compounds in the matrix spike and matrix spike duplicate samples. If the recovery of the matrix spike and duplicate are within the method-specified limits, then the method is judged to be applicable to that sample matrix. If, however, the recovery of the spike is not within the recovery range specified, either the method does not work on the sample, or the sample preparation process is out of control.

If the method is not appropriate for the sample matrix, then changes to the method are required. Matrix spike results are necessary in evaluating the modified method. If the analytical process is out of control, the laboratory must take immediate corrective action before any more samples are analyzed.

To separate indications of method performance from those of laboratory performance, the laboratory should prepare and analyze calibration verification standards and OPR samples. If the results for either of these analyses are not within the specified range, then the analytical system or process must be corrected. After the performance of the analytical system and processes have been verified (through the successful analysis of CCV and OPR samples), the spike sample analysis should be repeated. If the recovery of the matrix spike and duplicate are within the method-specified range, then the method and laboratory performance can be considered acceptable. If, however, the recovery of the matrix spike does not meet the specified range, the laboratory should attempt to further isolate the metal and repeat the test. If recovery of the metal remains outside the acceptance criteria, the data reviewer may apply the following guidelines when attempting to make use of the data:

- If the recovery of the matrix spike and duplicate are above method specifications but that metal is not detected in an associated sample or is detected below the regulatory compliance limit, then it unlikely that the sample result is affected by the failure in the matrix spike.

- If the recovery of the matrix spike and duplicate are above method specifications and that metal is detected in an associated sample above the regulatory compliance level, then the sample result may represent the upper limit of the true concentration, and the data should not be considered valid for regulatory compliance purposes.

- If the concentration of the matrix spike and duplicate are below method specifications but that metal is detected in an associated sample, then the sample result may represent the lower limit of the true concentration for that metal. If the metal was detected in the sample at a concentration higher than the regulatory compliance limit, then it is unlikely that the sample result is adversely affected by the matrix. If, however, the metal was detected below the regulatory compliance limit, the data should not be considered valid for regulatory compliance purposes.

10. Statements of Data Quality for Spiked Sample Results

The 1600 Series Analysis Methods specify that after the analysis of five spiked samples of a given matrix type, a statement of data quality is constructed for each analyte. The statement of data quality for each analyte is computed as the mean percent recovery plus and minus two times the standard deviation of the percent recovery for the analyte. The statements of data quality should then be updated by the laboratory after each five to ten subsequent spiked sample analysis.

The statement of data quality can be used to estimate the true value of a reported result and to construct confidence bounds around the result. For example, if the result reported for analysis of selenium is 10 ppb, and the statement of data quality for selenium is 84% ± 25% (i.e., the mean recovery is 84% and the standard deviation of the recovery is 25%), then the true value for selenium will be in the range of 9.4 - 14.4 ppb, with 95% confidence. This range is derived as follows:

$$\text{Lower Limit} = [(10 \div .84) - (10 \times .25)] = [11.9 - 2.5] = 9.4 \text{ ppb}$$
$$\text{Upper Limit} = [(10 \div .84) + (10 \times .25)] = [11.9 + 2.5] = 14.4 \text{ ppb}$$

Many laboratories do not provide the data quality statements with the sample results, in which case the data reviewer must determine if the data quality statements are being maintained for each analyte and may need to obtain the data. If necessary, the reviewer can construct the data quality statement from the individual data points. The lack of a data quality statement does not invalidate results but makes some compliance decisions more difficult. If statements of data quality are not being maintained by the laboratory, there may be increased concern about both specific sample results and the laboratory's overall quality assurance program.

11. Statements of Data Quality for Spiked Reagent Water Results

In addition to statements of data quality for results of analyses of the compounds spiked into field samples, the 1600 Series Analysis Methods require that statements of data quality be constructed from the initial and ongoing precision and recovery data. The purpose of these statements is to assess laboratory performance in the practice of the method, as compared to the assessment of method

performance made from the results of spiked field samples. Ideally, the two statements of data quality would be the same. Any difference could be attributable to either random error or sample matrix effects.

12. Field Duplicates

Method 1669 requires the collection of at least one field duplicate for each batch of field samples collected from the same site. The field duplicate provides an indication of the overall precision associated with entire data gathering effort, including sample collection, preservation, transportation, storage, and analysis procedures. The data reviewer should examine field duplicate results and use the following equation to calculate the relative percent difference between the duplicate and its associated samples.

$$RPD = 200\frac{(|D1-D2|)}{(D1+D2)}$$

where:
D1 = concentration of the analyte in the field sample
D2 = concentration of the analyte in the duplicate field sample

If the analyte of interest was not detected in either replicate of the field sample, then the RPD will be zero. If the analyte was detected in each field sample replicate, but the results are highly disparate (indicated by a large RSD), the reviewer should apply the following guidelines when making use of the data:

- If the analyte was detected in each replicate and at similarly variable concentrations in the blank samples, then the field sample variability may be attributable to variable contamination, and the data may not be valid for regulatory compliance purposes.

- If the analyte was detected in each replicate at a concentration well above the regulatory compliance level, but was not detected in the associated blank samples, then it is likely that the sample results are not adversely affected.

Ideally, the RPD between field duplicates and MS/MSD samples will be identical. Any difference between the two is attributable to variability associated with the field sampling process.

Chapter 4

Data Inspection Checklist

The following pages contain a data inspection checklist that may be used by data reviewers, laboratory personnel, and other parties to document the results of each data inspection in a standardized format.

Summary Information

1. Name of Reviewer: _____ Title: _____

Required Samples		Sample Results Provided	
Sample Location or Sample ID	Analyte(s)	Sample Location or Sample ID	Analyte(s)

2. Method Used:

3. Total No. of analytical shifts per instrument (determined from analysis run log):

Instrument — No. of Shifts

4. Total No. of CCVs Required: _____ Total No. of CCVs Reported: _____
(one for each 10 samples after the first 10 samples on each instrument)

5. Total No. of CCBs Required: _____ Total No. of CCBs Reported: _____
(one for each CCV)

6. Total No. of Field Blanks Required: _____ Total No. of Field Blanks Reported: _____
(one per site or per 10 samples, whichever is more frequent)

7. Total no. of Lab Blanks Required: _____ Total No. of Lab Blanks Reported: _____
(one per batch* per method/instrument)

8. Total no. of OPR analyses Required: _____ Total No. of OPR Analyses Reported: _____
(one per batch per method/instrument)

9. Total no. of MS/MSD samples Required: _____ Total No. of MS/MSD samples Reported: _____
(one per 10% per matrix per site)

10. Total no. Field Duplicates Required: _____ Total No. of Field Duplicates Reported: _____
(one per 10 samples per site)

11. Total no. of MDL results required: _____ Total No. of MDL Results Reported: _____
(one per method and per analyte)

12. Initial Calibration

a. Was a multiple point initial calibration performed*? ☐yes ☐no

b. Were all sample concentrations reported within the calibration range? ☐yes ☐no

If no, list method and analytes for which initial calibration was not performed or which exceeded the calibration range.

c.

Analyte	No ICAL (Y/N)	Exceeded ICAL Range (Y/N)

d. Did the initial calibration meet linearity criteria? ☐yes ☐no

e. If no, was a calculation curve used to calculate sample concentrations? ☐yes ☐no

* A three point (minimum) initial calibration should be performed for each analyte; if the RSD of the mean RRF is less than 15%, or if the RSD of the mean RF is less than 25%, then the averaged RRF or RF, respectively, may be used for that analyte.

13. Method Detection Limit (MDL)/Minimum Level (ML)

a. Did the laboratory demonstrate their ability to achieve the required MDL? ☐yes ☐no

b. Did the initial calibration range encompass the ML? ☐yes ☐no

c. Were all field samples detected below the ML reported as non-detects? ☐yes ☐no

d. If the answer to item a, b, or c above was "no", describe problem:

14. Initial Calibration Verification (ICV)/Initial Calibration Blanks (ICB):

a. Was an ICV run prior to field samples? ☐yes ☐no

b. Were ICV results within the specified windows? ☐yes ☐no

c. Was the ICV followed by an ICB? ☐yes ☐no

d. Was the ICB free from contamination? ☐yes ☐no

e. If any item in a - d above was answered "no", list problems below:

Analyte	Failed ICV Recovery	Concentration Detected in ICB	Affected Samples

15. Initial Precision and Recovery (IPR)

a. Were IPR data reported for each analyte? ☐yes ☐no

b. Did all IPR aliquots meet required recovery criteria (x)? ☐yes ☐no

c. Did the standard deviation (s) of each IPR series meet the required criterion? ☐yes ☐no

d. If any item in a - c above was answered "no", document problem below.

Analyte	Ave. Result Reported (X)	RSD Reported	Affected Samples

16. Ongoing Precision and Recovery (OPR)

a. Were OPR data reported for each analyte, instrument, and batch? ☐yes ☐no

b. Did all OPR samples meet required recovery criteria (x)? ☐yes ☐no

c. If item a or b above was answered "no", document problem below.

Analyte	OPR Recovery (X) Reported	Shifts Missing OPR	Affected Samples

17. Continuing Calibration Verification (CCV)/Continuing Calibration Blank (CCB)

a. Were CCVs run prior to each batch of 10 samples on each instrument? ☐yes ☐no

b. Were all CCV results within the specified windows? ☐yes ☐no

c. Was each CCV followed by a CCB? ☐yes ☐no

d. Was each CCB free from contamination? ☐yes ☐no

e. If any item in a - d above was answered "no", list problems below:

Analyte	Affected Samples	Shift Missing CCV/CCB	Failed CCV/CCB ID

18. Laboratory (Method) Blanks

a. Was a method blank analyzed for each instrument & sample batch? ☐yes ☐no

b. Was each method blank demonstrated to be free from contamination? ☐yes ☐no

c. If the answer to item a or b was "no", document problems below.

Analyte	Affected Samples	Blank Concentration Reported	Shift Missing MB

19. Field Blanks

a. Was a field blank analyzed for each 10 samples per site? ☐yes ☐no

b. Was each field blank demonstrated to be free from contamination? ☐yes ☐no

c. If the answer to item a or b was "no", document problems below.

Analyte	Affected Samples	Blank Concentration Reported	Shift Missing FB

20. MS/MSD Results

a. Were appropriate number of MS/MSD pairs analyzed? ☐yes ☐no

b. Were all MS/MSD recoveries within specified windows? ☐yes ☐no

c. Were all RPDs within the specified window? ☐yes ☐no

d. Was appropriate corrective action (e.g., MSA for GFAA, serial dilution for ICP) employed on affected samples? ☐yes ☐no

e. If the answer was "no" to items a - d above, document affected samples:

Analyte	MS % R	MSD % R	MS/MSD RPD	Affected Samples

21. Additional Information

a. Were Instrument Tune Data Provided? ☐yes ☐no

b. Were equipment blanks demonstrated to be free from contamination? ☐yes ☐no

c. Were statements of data quality provided? ☐yes ☐no

d. Did field duplicate demonstrate acceptable precision? ☐yes ☐no

Glossary

Accuracy: The degree of agreement between a measured value and the true or expected value of the quantity of concern.

Calibration Blank: A sample of reagent water analyzed after the calibration verification standard to check for contamination attributable to the analytical system.

Calibration Range (Calibration Curve): A graphical relationship between the known values for a series of calibration standards and instrument responses, specifically the linear portion of this relationship between calibration standards.

Dissolved Metals: The concentration of metal(s) that will pass through a 0.45 micron filter assembly, prior to acidification of the sample.

Equipment Blank: An aliquot of reagent water that is subjected in the laboratory to all aspects of sample collection and analysis, including contact with all sampling devices and apparatus. The purpose of the equipment blank is to determine if the sampling devices and apparatus for sample collection have been adequately cleaned prior to shipment to the field site. An acceptable equipment blank must be achieved before the sampling devices and apparatus are used for sample collection.

Field Blank: An aliquot of reagent water that is placed in a sample container in the laboratory, shipped to the sampling site, and treated as a sample in all respects, including contact with the sampling devices and exposure to sampling site conditions, storage, preservation, and all analytical procedures, which may include filtration. The field blank is used to determine if field sample handling processes, sample transport, and sampling site environment have caused sample contamination.

Field Duplicates: Two identical aliquots of a sample collected in separate sample containers at the same time and place under identical circumstances and sample collection techniques, and handled in exactly the same manner as other samples. Field duplicates are used as a measure of the precision associated with sample handling, preservation, and storage as well as laboratory handling, preparation, and analytical procedures.

Initial Precision and Recovery (IPR): A series of four consecutively analyzed aliquots of reagent water containing the analyte(s) of interest at 2 - 3 times the ML. IPRs are performed prior to the first time a method is used and any time the method or instrumentation is modified. The IPR is used to demonstrate the analyst/laboratory ability to generate acceptable precision and accuracy through the calculated mean (x) and standard deviation (s) for each analyte.

Laboratory Blank: An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. the laboratory blank is used to determine if analytes or interferences are present in the laboratory environment, reagents, or the apparatus.

Magnetic Media: A storage medium on which all instrumentally acquired raw data may be retained.

Matrix Spike (MS) and Matrix Spike Duplicate (MSD): Aliquots of an environmental sample to which known quantities of analytes are added in the laboratory. The MS and MSD are analyzed under the same conditions as other samples and are used to quantify the bias and precision associated with the sample matrix. The background concentration of the analytes in the sample are determined and subtracted from the MS and MSD results.

Method Blank: See "laboratory blank".

Method Detection Limit (MDL): The minimum concentration of an analyte that, in a given matrix and with a specified method, has a 99% probability of being identified, qualitatively or quantitatively measured, and reported to be greater than zero.

Minimum Level (ML): The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point.

Ongoing Precision and Recovery (OPR): An aliquot of reagent water containing the analyte(s) of interest. The OPR is used to demonstrate continuing ability of the analyst/laboratory to generate acceptable results based on target and standard recoveries.

Quality Assurance (QA): An integrated system of activities involving planning, quality control, quality assessment, reporting, and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

Quality Control (QC): The overall system of technical activities designed measure and control the quality of a product or service so that it meets the needs of users. The aim is to provide quality that is satisfactory, adequate, dependable, and economical.

Precision: The degree of mutual agreement characteristic of independent measurements as the result of repeated applications of the process under specified conditions.

Reagent Water: Water demonstrated to be free from the metal(s) of interest at the method detection limit (MDL) of the analytical method to be used for determination of the metal(s) of interest.

Reference Standards: A material or substance, one or more properties of which are sufficiently well established to be used for the calibration of analytical apparatus, the assessment of a measurement method, or assigning of values to materials.

Trace Metals: Concentrations of metals found at or near their established water quality criteria levels.

Appendix A

EPA Water Quality Criteria for Priority Pollutant Metals and Metals Species

The table provided on the following page provides the freshwater, marine, and human health water quality criteria published by EPA for priority pollutant metals and metals species. This table includes criteria for both total recoverable metals and dissolved metals. Criteria for dissolved metals were calculated in accordance with an October 1, 1993 guidance memorandum transmitted by the Acting Assistant Administrator for Water to Water Management Division Directors and Environmental Services Division Directors. This table also includes freshwater criteria that are based on a hardness of 100 mg/L. These values were published by EPA in the National Toxics Rule at 57 *FR* 60848. In order to provide a worst-case scenario, the table also includes criteria that are based on a hardness of 25 mg/L $CaCO_3$. Calculations for deriving these values were published by EPA in the National Toxics Rule.

EPA Ambient Water Quality Criteria for Total Recoverable and Total Dissolved Priority Pollutant Metals and Metal Species Calculated at a Hardness of 100 mg/L and 25 mg/L $CaCO_3$

Metal	Ambient Water Quality Criteria[1] (µg/L)													
	Freshwater Criteria								Marine Criteria				Human Health Criteria	
	Acute[2] Tot. Rec. 100 mg/L $CaCO_3$	Acute[3] Tot. Diss. 100 mg/L $CaCO_3$	Acute[4] Tot. Rec. 25 mg/L $CaCO_3$	Acute[3],[4] Tot. Diss. 25 mg/L $CaCO_3$	Chronic[2] Tot. Rec. 100 mg/L $CaCO_3$	Chronic[3] Tot. Diss. 100 mg/L $CaCO_3$	Chronic[4] Tot. Rec. 25 mg/L $CaCO_3$	Chronic[3],[4] Tot. Diss. 25 mg/L $CaCO_3$	Acute[2] Tot. Rec.	Acute[3] Tot. Diss.	Chronic[2] Tot. Rec.	Chronic[3] Tot. Diss.	H_2O/organism[2] Tot. Rec.	organism[3] Tot. Rec.
Sb	---	---	---	---	---	---	---	---	---	---	---	---	*14*[5]	4300[5]
As	360	342	360	342	190	181	190	181	69	65.6	36	34.2	*0.018*[5]	0.14[5]
Cd[6]	3.9	3.3	0.82	0.70	1.1	0.94	0.38	*0.32*	43	36.6	9.3	7.9	---	---
Cr (III)[6]	1700	1450	560	476	210	179	67	*57*	---	---	---	---	---	---
Cr (VI)	16	15.2	16	15.2	11	*10.5*	11	*10.5*	1100	1050	50	47.5	---	---
Cu[6]	18	15.3	4.8	4.1	12	10.2	3.6	3.1	2.9	*2.5*	2.9	*2.5*	---	---
Pb[6]	82	41	14	7	3.2	0.8	0.54	*0.14*	220	110	8.5	2.1	---	---
Hg	2.4	2.0	2.4	2.0	*0.012*	---[7]	*0.012*	---[7]	2.1	1.8	0.025	---[7]	0.14	0.15
Ni[6]	1400	1190	440	374	160	136	49	42	75	64	8.3	*7.1*	610[5]	4600[5]
Se	20	---[7]	20	---[7]	*5*	---[7]	*5*	---[7]	300	---[7]	71	---[7]	---	---
Ag[6]	4.1	3.5	0.37	*0.31*	---	---	---	---	2.3	2.0	---	---	---	---
Tl	---	---	---	---	---	---	---	---	---	---	---	---	*1.7*[5]	6.3[5]
Zn[6]	120	102	36	31	110	94	33	*28*	95	81	86	73	---	---

(1) WQC promulgated in the National Toxics Rule (NTR) for 14 states at 40 *CFR* Part 131 (57 FR 60848). Critria for metals listed at 40 *CFR* Part 131 are expressed as total recoverable at a hardness of 100 mg/L $CaCO_3$ and a water effect ratio (WER) of 1.0. The lowest WQC for each analyte is shaded.

(2) As listed in the NTR at 40 *CFR* Part 131 for total recoverable metals. Hardness dependent freshwater acute and chronic criteria expressed at a hardness of 100 mg/L $CaCO_3$ and a WER of 1.0.

(3) For Cd, Cr (III), Cu, Ni, and Zn, acute and chronic criteria for dissolved metals and metal species were calculated by taking 85% of the corresponding total recoverable criteria level. For As and Cr (VI), acute and chronic criteria for dissolved metals and metal species were calculated by taking 95% of the corresponding total recoverable criteria level. For lead, acute dissolved criteria were calculated by taking 50% of the corresponding total recoverable level; for lead chronic criteria, dissolved criteria were calculated by taking 25% of the total recoverable levels. Dissolved values for mercury chronic criteria and selenium acute and chronic criteria were not calculated because these metals bioaccumulate, and dissolved criteria would not be appropriate. (*Guidance Document on Dissolved Criteria: Expression of Aquatic Life Criteria*, October 1993. Attachment 2 to memorandum from Martha Prothro to Water Management Division Directors, October 1, 1993.)

(4) Hardness dependent freshwater acute and chronic criteria recalculated at a hardness of 25 mg/L $CaCO_3$ and a WER of 1.0 as specified at 40 *CFR* Part 131.36 (b)(2). For dissolved metals, hardness calculations were performed prior to adjusting for dissolved levels.

(5) Criterion reflects recalculated value using IRIS.

(6) Freshwater criteria are hardness dependent for this metal.

(7) Metal is bioaccumulative and, therefore, it is not appropriate to calculate WQC for dissolved levels. (*Guidance Document on Dissolved Criteria: Expression of Aquatic Life Criteria*, October 1993. Attachment 2 to memorandum from Martha Prothro to Water Management Division Directors, October 1, 1993.)