# EPA DRINKING WATER METHOD FORMAT

Each method should be a free-standing document, providing all information necessary for the method user to perform the method. References within a method should be restricted to associated or source material. Procedural steps or instructions should not be referenced as being found elsewhere, but should be included in totality within the method.

## General Formatting

- EPA drinking water methods are required to meet relevant 508 compliance standards for EPA publications
- An author page should appear after the title page listing the EPA contact information, relevant method authors, and acknowledgment of parties that participated in the development of the method.
- A Table of Contents should appear after the author and acknowledgments page.
- Page Numbering. Page numbers should appear at the bottom center of each page.
- Font. Use at least an 11-point font size. Choice of font should be limited to those that are Adobe®-supported since methods will be converted to .pdf format when submitted for the OGWDW web page.
- Single space document. Insert a blank line between each paragraph and section.
- Section headings and numbering. Use the Modified Decimal Numbering (MDN) system to organize material presented in methods. In this system, each method section and subsection is assigned a unique number that shows the relationship of a specific section/subsection to all previous sections/subsections and allow for easy reference. The first-order headings are described in the 17 method sections (1.0, 2.0, 3.0, etc.). Second- order headings are then numbered 1.1, 1.2, 1.3, etc. Third-order headings are numbered 1.1.1, 1.1.2, 1.1.3, etc. Fourth-order headings are numbered 1.1.1.1, 1.1.1.2, 1.1.1.3, etc. Use of subdivisions beyond the fourth-order should be avoided where possible by organizing the material differently. Each of these numbered sections should have a short heading that summarizes that section.
- All sections should begin from the leftmost margin.
- References. Use the following format when listing references:
    - Books: Author's name/names (last name, initials), title of book (underline, no quotation marks). Name of publisher, address of publisher (city, state), year of publication, page number (if applicable).
    - Journals: Author's name/names (last name, initials), "title of paper" (quotation marks), *name of journal* (italics), volume number, issue number (omit if journal page numbers are continuous throughout the volume), year of publication, page numbers.
    - Proceedings, transactions, reports, bulletins, etc.: Author's name/names (last name, initials), "title of paper" (quotation marks), name of publication (underline, no quotation marks), name of publisher, volume number, date of publication, page numbers.
    - Symposium volumes or other books containing collections of papers: follow the style for books, except add the title of the paper (in quotation marks) after the author's name.
    - Patents: Patent number and date

    - EPA Methods: Method number and name, EPA document number, U.S. Environmental Protection Agency, laboratory and/or office, location, date.
- Use commonly accepted acronyms and abbreviations in text and tables. Always spell out the term the first time it is used and follow it with the acronym or abbreviation in parentheses, e.g., relative percent difference (RPD).

**EPA Drinking Water Method Sections**

EPA analytical methods contain the following 17 required sections. Guidelines are presented below for each section. Since methods differ in complexity and scope, most "boiler plate" language is limited to the definitions (Sect. 3) and quality control (Sect. 9).

## 1.0 Scope and Application

This section describes the purpose, analytical range, limitations, intended use of the method, and identifies the analytes. Specify the list of analytes that can be evaluated using the method, including each analyte's Chemical Abstracts Service Registry Number. The use of acceptable common names of pesticides and other registered trademark names is permitted. Identify the drinking water matrixes in which method performance was found to be acceptable. Indicate the reporting levels and detection limits for the method.

In recognition of technological advances in analytical systems and techniques, this Section should also briefly describe boundaries within which any method modifications will be permitted (e.g., the use of alternate GC/LC columns, alternate analytical operating parameters, etc.). Note: Changes may not be made to sample collection and preservation (Sect. 8), sample extraction (if applicable), or to the Quality Control (QC) requirements (Sect. 9). Method modifications should be considered only to improve method performance. Modifications that are introduced in the interest of reducing cost or sample processing time, but result in poorer method performance, may not be used. In all cases where method modifications are proposed, the analyst must perform the procedures outlined in the initial demonstration of capability (IDC, Sect. 9), verify that all QC acceptance criteria in the method are met, and that method performance in real sample matrixes is equivalent to that demonstrated for Laboratory Fortified Sample Matrixes (LFSMs) compiled in data tables in Sect. 17.

## 2.0 Summary of Method

This section provides an overview of the method procedure and quality assurance. Describe the basic steps involved in performing the method, e.g., describe the techniques that are used (solid phase extraction, gas chromatography, liquid chromatography, mass spectrometry, etc.). Briefly describe how quality is assured (e.g., calibration and quantitation using internal standardization, comparison of acquired mass spectra and retention times to reference spectra and retention times for calibration standards acquired under identical conditions, etc.).

## 3.0 Definitions

This section includes definitions of terms, acronyms, and abbreviations used in the method. If preferred, definitions may be provided in a glossary at the end of the method or manual. In this case, the definitions section should still appear in the method, with a notation that they are provided in a glossary at the end of the method.

The following definitions are common to many of the drinking water methods but may not be applicable to a specific method. As appropriate, the analyst can modify these definitions for additional clarity as it relates to a specific method:

ANALYSIS BATCH - A set of samples that is analyzed on the same instrument during a 24-hour period that begins and ends with the analysis of the appropriate Continuing Calibration Check (CCC) Standards. Additional CCCs may be required depending on the length of the analysis batch and/or the number of field samples

CONTINUING CALIBRATION CHECK (CCC) - A calibration standard which is analyzed periodically to verify the accuracy of the existing calibration for those analytes.

DETECTION LIMIT (DL), also called METHOD DETECTION LIMIT (MDL) - The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. This is a statistical determination, and accurate quantitation is not expected at this level. (*See References Section 16, includes the DL citation*).

FIELD REAGENT BLANK (FRB) - An aliquot of reagent water or other blank matrix that is shipped to the field sampling site, where it is poured into a separate FRB sample bottle and shipped back to the laboratory for analysis. The FRB is treated as a sample in all respects, including shipment to/from the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

EXTRACTION BATCH - A set of up to 20 Field Samples (not including QC samples) extracted together by the same person(s) during a work day using the same lot of solid phase extraction devices, solvents, surrogate solution, and fortifying solutions. Required QC samples include Laboratory Reagent Blank, Laboratory Fortified Blank, Laboratory Fortified Sample Matrix, and either a Field Duplicate or Laboratory Fortified Sample Matrix Duplicate

INTERNAL STANDARD (IS) - A pure compound added to an extract or standard solution in a known amount and used to measure the relative responses of the method analytes and surrogates. The internal standard must respond similarly to the method analytes, have no potential to be present in water samples, and not be a method analyte.

LABORATORY FORTIFIED BLANK (LFB) - An aliquot of reagent water or other blank matrix to which known quantities of the method analytes and all the preservation compounds are added. The LFB is processed and analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

LABORATORY FORTIFIED SAMPLE MATRIX (LFSM) - An aliquot of a preserved field sample to which known quantities of the method analytes are added. The LFSM is processed and analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFSM corrected for background concentrations.

LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (LFSMD) - A duplicate preserved field sample used to prepare the LFSM, which is fortified, extracted and analyzed identically to the LFSM. The LFSMD is used instead of a Field Duplicate to assess method precision and accuracy when the occurrence of a method analyte is infrequent.

LABORATORY REAGENT BLANK (LRB) - A volume of reagent water or other blank matrix that is processed exactly as a sample including exposure to all glassware, equipment, solvents and reagents, sample preservatives, surrogates and internal standards that are used in the extraction and analysis batches. The LRB is used to determine if the method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

LOWEST CONCENTRATION MINIMUM REPORTING LEVEL (LCMRL) - The single laboratory LCMRL is the lowest true concentration for which the future recovery is predicted to fall between 50% to 150% with 99% confidence.[1] (*See References Section 16.0, includes the LCMRL citation*).

MINIMUM REPORTING LEVEL (MRL) - The minimum concentration that can be reported by a laboratory as a quantitated value for a method analyte in a sample following analysis. This concentration must meet the criteria defined in Sect. 9 (*MRL confirmation procedure as specified in QC Section 9)* and must not be any lower than the concentration of the lowest continuing calibration check standard for that analyte.

PRIMARY DILUTION STANDARD (PDS) - A solution containing method analytes, internal standards, or surrogate analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other analyte solutions.

QUALITY CONTROL SAMPLE (QCS) - A solution containing the method analytes at a known concentration that is obtained from a source external to the laboratory and different from the source of calibration standards. The purpose of the QCS is to verify the accuracy of the primary calibration standards.

STOCK STANDARD SOLUTION (SSS) - A concentrated standard solution that is prepared in the laboratory using assayed reference materials or that is purchased from a commercial source with a certificate of analysis.

SURROGATE ANALYTE (SUR) - A pure chemical which is unlikely to be found in any sample, and which is added to a sample volume in a known amount before extraction. Surrogates are evaluated using the same procedures as other sample components. Because surrogates are present in every sample, they provide a means of assessing method performance for each sample extraction.

TRIP BLANK - A clean sample of a matrix that is taken from the laboratory to the sampling site and transported back to the laboratory without having been exposed to sampling procedures. The sample is not opened in the field. (Typically required when analyzing for volatile compounds.) The purpose of the trip blank is to assess contamination

introduced during shipping and storage

**4.0 Interferences**

This section identifies known or potential interferences that may occur during use of the method and describes ways to reduce or eliminate interferences.

**5.0 Safety**

This section describes special precautions needed to ensure personnel safety during the performance of the method. Procedures described here should be limited to those which are above and beyond good laboratory practices. The section should contain information regarding specific toxicity of analytes or reagents.

**6.0 Equipment and Supplies**

This section lists and describes all non-consumable supplies and equipment needed to perform the method. As much as practical, strive to identify supplies and equipment in generic terms. Include a general statement such as: “References to specific brands or catalog numbers are included as examples only and do not imply endorsement of the product. Such reference does not preclude the use of other vendors or suppliers.”

**7.0 Reagents and Standards**

This section lists and describes all reagents and standards that are required to perform the procedures described in the method and provides preparation instructions or suggested suppliers as appropriate. As with equipment and supplies, try to identify reagents and standards in generic terms.

**8.0 Sample Collection, Preservation, and Storage**

This section provides requirements and instructions for collecting, preserving, and storing samples. Include specifications for sample containers (e.g., plastic/glass, volume requirements). Include temperature ranges required for shipment and storage. Include holding time criteria for samples and extracts (if samples are extracted).

**9.0 Quality Control**

This section cites the procedures and analyses required to fully document the quality of data generated by the method. The required components of the laboratory's quality assurance (QA) program and specific quality control (QC) analyses appropriate to the method are described in this section. Provide a detailed description of the initial demonstration of capability (IDC) including: demonstration of low system background, precision, accuracy, and confirmation of the minimum reporting level (MRL). Provide instructions regarding ongoing QC requirements: blanks, continuing calibration checks, internal standards, extraction surrogates, matrix spikes and matrix spike duplicates.

QC language and criteria differ between organic and inorganic (primarily metals) methods and are described separately.

**The following procedures are common to the drinking water methods primarily for the analysis of organic contaminants, though they also apply to the analysis of inorganic contaminants using ion chromatography.** Note: The QC requirements in this

section are considered the minimum acceptable QC criteria. Laboratories are encouraged to institute additional QC practices to meet their specific needs.

INITIAL DEMONSTRATION OF CAPABILITY (IDC). The IDC must be successfully performed prior to analyzing any field samples. Prior to conducting the IDC, the analyst must generate an acceptable initial calibration following the procedure outlined in Section 10. *(The IDC consists of the following: demonstration of low system background, demonstration of precision and accuracy, MRL confirmation, QCS analysis, and if required by regulation, MDL determination as described in 40 CFR 136, Appendix* $B^2$).

DEMONSTRATION OF LOW SYSTEM BACKGROUND. Analyze an LRB. Confirm
that the blank is free of contamination.

INITIAL DEMONSTRATION OF PRECISION. Prepare, extract (*if extraction is part of the procedure)* and analyze four to seven replicate LFBs. Fortify these samples near the midrange of the initial calibration curve. The method preservatives must be added to the LFBs as described in Section 8. Confirm the relative standard deviation (%RSD) meets the specified QC criterion (*unless otherwise noted, %RSD* $\leq$ *20%).*

INITIAL DEMONSTRATION OF ACCURACY. Using the same set of replicate data generated for the Initial Demonstration of Precision, calculate the average percent recovery. Confirm the average percent recovery for each analyte meets the specified QC criterion (*unless otherwise notes, % recovery is ±30% of the true value*).

MINIMUM REPORTING LEVEL (MRL) CONFIRMATION. Establish a target concentration for the MRL based on the intended use of the method. Analyze an initial calibration following the procedures in Section 10. The lowest calibration standard used to establish the initial calibration (as well as the low-level CCC) must be at or below the concentration of the MRL. Establishing the MRL concentration too low may cause repeated failure of ongoing QC requirements. Confirm the MRL following the procedure: Fortify, extract (*if extraction is part of the procedure),* and analyze seven replicate LFBs at or below the proposed MRL concentration. The LFBs must contain the method preservatives as specified in Section 8. Calculate the mean (*Mean*) and standard deviation for these replicates. Determine the Half Range for the Prediction Interval of Results ($HR_{PIR}$) where $HR_{PIR} = 3.963S$. *S* is the standard deviation and 3.963 is a constant value for seven replicates. Confirm that the Upper and Lower limits for the Prediction Internal of Results ($PIR = Mean \pm HR_{PIR}$) meet the required recovery limits: The Upper PIR Limit [$(Mean + HR_{PIR})/(Fortified\ Concentration) \times 100$] must be $\leq$ 150% and the Lower PIR Limit [$(Mean - HR_{PIR})/(Fortified\ Concentration) \times 100$] must be $\geq$ 50%. The MRL is validated if both the Upper and Lower PIR Limits meet the criteria described. If these criteria are not met, the MRL has been set too low and must be confirmed again at a higher concentration.

QUALITY CONTROL SAMPLE (QCS). Analyze a mid-level QCS to confirm the accuracy of the primary calibration standards.

ONGOING QC REQUIREMENTS. This describes the ongoing QC elements that must be included when processing and analyzing field samples.

LABORATORY REAGENT BLANK (LRB). An LRB is required with each analysis batch to confirm that potential background contaminants are not interfering with the identification or quantitation of target analytes. If the LRB produces a signal that would prevent the determination of an analyte, locate the source of contamination and eliminate the interference before processing samples. Background contamination must be reduced to an acceptable level before proceeding. *(Acceptance criteria are defined in the method).*

CONTINUING CALIBRATION CHECK (CCC). Analyze a CCC to verify the initial calibration at the beginning of each analysis batch, after every tenth field sample, and at the end of each analysis batch. The beginning CCC for each analysis batch must be at or below the MRL. This CCC verifies instrument sensitivity prior to the analysis of samples. Subsequent CCCs should alternate between a medium and high concentration calibration standard. *(Acceptance criteria are defined in the method).*

LABORATORY FORTIFIED BLANK (LFB). An LFB is required with each extraction batch. The fortified concentration of the LFB must be rotated between low, medium, and high concentrations from batch to batch. The low concentration LFB must be as near as practical to, but no more than two times the MRL. Similarly, the high concentration LFB should be near the high end of the calibration range established during the initial calibration. *(Acceptance criteria are defined in the method).*

INTERNAL STANDARDS (IS). The analyst must monitor the peak areas of the ISs in all injections during each analysis day. The peak area for each IS in any chromatographic run must not deviate by more than ±50% from the mean response in the CAL solutions analyzed for the initial calibration.

SURROGATE RECOVERY (*If method incorporates one or more surrogates*). Surrogate standards are fortified into all field samples, LRBs, LFBs, CCCs, LFSMs, and LFSMDs prior to extraction. They are also added to the calibration standards. The surrogates are a means of assessing method performance from extraction to final chromatographic measurement. Confirm the percent recovery of each surrogate meets the specified QC criteria (*unless otherwise noted, % recovery is ±30% of the true value*).

LABORATORY FORTIFIED SAMPLE MATRIX (LFSM). Within each analysis batch analyze a minimum of one LFSM for every 20 field samples. The background concentrations of the analytes in the sample matrix must be determined in a separate

aliquot and subtracted from the measured values in the LFSM. Confirm the percent recovery of each analyte meets the specified QC criteria. (*Acceptance criteria are defined in the method*).

FIELD DUPLICATE (FD) OR LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (LFSMD). Within each analysis batch analyze a minimum of one FD or LFSMD for every 20 field samples. Duplicates check the precision associated with sample collection, preservation, storage, and laboratory procedures. If target analytes are not routinely observed in field samples, an LFSMD should be analyzed rather than an FD. Calculate the relative percent difference (RPD) for duplicate measurements (either FD1 and FD2, or LFSM and LFSMD). Confirm the RPD meets the specified QC criteria. (*Acceptance criteria are defined in the method*).

QUALITY CONTROL SAMPLE (QCS). As part of the IDC, each time a new analyte PDS is prepared, and at least quarterly, analyze a QCS sample from a source different from the source of the CAL standards. If a second vendor is not available, then a different lot of the standard should be used. The QCS should be prepared and analyzed just like a CCC. Acceptance criteria for the QCS are identical to the CCCs.

METHOD MODIFICATION QC REQUIREMENTS. Each time method modifications (as discussed in Sect. 1) are made, the analyst must repeat the procedures of the IDC and verify that all QC criteria can be met in ongoing QC samples. Each time method modifications are made, the analyst is also required to evaluate and document method performance for the proposed method modifications in real matrixes that span the range of waters that the laboratory analyzes. This additional step is required because modifications that perform acceptably in the IDC, which is conducted in reagent water, can fail ongoing method QC requirements in real matrixes. This is particularly important for methods subject to matrix effects. If, for example, the laboratory analyzes finished waters from both surface and groundwater municipalities, this requirement can be accomplished by assessing precision and accuracy in a fortified surface water with moderate to high TOC (e.g., 2 mg/L or greater) and a fortified hard groundwater (e.g., 250 mg/L or greater as calcium carbonate). The results of the IDC and real matrix studies must be appropriately documented by the analyst and should be independently assessed by the laboratory's Quality Assurance (QA) officer prior to analyzing field samples. When implementing method modifications, it is the responsibility of the laboratory to closely review the results of ongoing QC, and in particular, the results associated with the LFSMs, FDs or LFSMDs, CCCs, and the IS area counts. If repeated failures are noted, the modification must be abandoned.

**The following procedures are common to the drinking water methods for the analysis of inorganic (primarily metals) contaminants.**

INITIAL DEMONSTRATION OF PERFORMANCE. The initial demonstration of performance is used to characterize instrument performance (determination of linear dynamic ranges and analysis of quality control samples) and laboratory performance (determination of method detection limits) prior to samples being analyzed by this method.

LINEAR DYNAMIC RANGE (LDR). The upper limit of the LDR must be established (it is a detector-limited parameter and each method defines the appropriate procedure).

QUALITY CONTROL SAMPLE (QCS). When beginning use of a method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with preparation and analysis of a QCS. *(Acceptance criteria are defined in the method).*

METHOD DETECTION LIMIT (MDL). MDLs are established for all analytes using reagent water (blank) fortified at a concentration of two to three times the estimated
instrument detection limit and following the procedure described at 40 CFR 136, Appendix B. MDLs should be determined annually, when a new operator begins work or when, in the judgement of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

ASSESSING LABORATORY PERFORMANCE. This section describes the ongoing QC elements that must be included when processing and analyzing field samples.

LABORATORY REAGENT BLANK (LRB). The laboratory must analyze at least one LRB with each batch of 20 or fewer samples of the same matrix. LRB data are used to assess contamination from the laboratory environment. *(Acceptance criteria are defined in the method).*

LABORATORY FORTIFIED BLANK (LFB). The laboratory must analyze at least one LFB with each batch of samples. *(Acceptance criteria are defined in the method).*

INSTRUMENT PERFORMANCE CHECK (IPC) SOLUTION. The IPC solution is prepared in the same acid diluent as the calibration standards by adding the method analytes at appropriate concentrations to approximate the midpoint of the calibration curve (*i.e., the IPC is equivalent to a CCC as described for the organic methods*). The lab must analyze an IPC and a calibration blank (*the acid diluent used to prepare the calibration standards*) immediately following each calibration, after every $10^{th}$ sample
and at the end of the sample run. (Acceptance criteria are defined in the method).

LABORATORY FORTIFIED MATRIX (LFM). The lab must add a known amount of each analyte to a minimum of 10% of the routine samples (*unless otherwise specified by the data user, laboratory, or program*). *(Acceptance criteria are defined in the method).*

INTERNAL STANDARDS RESPONSES. If internal standards are incorporated, the analysis is expected to monitor the responses of the internal standards. Ratios of

internal standards responses against each other should also be routinely monitored. *(Acceptance criteria are defined in the method).*

**10.0 Calibration and Standardization**

This section describes the method/instrument calibration and standardization process and the required calibration verification. Provide detailed instructions regarding the use of standards to prepare the calibration curve. Include the minimum number of calibration standards, acceptance criteria, frequency of calibration checks (CCCs), etc. As appropriate, describe the use of internal standardization, including the number and concentration levels of internal standards. Include instructions regarding the stability and storage of calibration standard solutions. Corrective actions should be described for cases when performance specifications are not met.

**11.0 Procedure**

This section describes the sample processing and instrumental analysis steps of the method and provides detailed instructions to analysts. Include in proper sequence the detailed directions for sample preparation, extraction (if employed), and analysis.

**12.0 Data Analysis and Calculations**

This section provides instructions for analyzing data, equations, and definitions of constants used to calculate final sample analysis results and their uncertainties. Under no circumstances is an analyst permitted to extrapolate beyond the established calibration; the method must note that analyses that exceed the calibration range require dilution and re-injection.

**13.0 Method Performance**

This section provides method performance criteria for the method, including precision and accuracy statements regarding application of the method to multiple matrixes (e.g. reagent water, finished drinking waters drawn from various source waters, high ionic strength water, etc.), the detection levels, and sources and limitations of data produced using the method. Describe how the method was validated and report the number of participating operators/laboratories.

**14.0 Pollution Prevention**

This section describes aspects of the method that minimize or prevent pollution known to be or potentially attributable to the method.

**15.0 Waste Management**

This section describes minimization and proper disposal of waste and samples.

**16.0 References**

This section lists references for source documents and publications that contain ancillary information. Drinking water methods cite both LCMRL and MDL determinations:

1. Winslow, S.D.; Pepich, B.V.; Martin, J. J.; Hallberg, G.R.; Munch D.J.; Frebis, C.P.; Hedrick, E.J.; Krop, R.A. Statistical Procedures for Determination and Verification of Minimum Reporting Levels for Drinking Water Methods. *Environ. Sci. Technol*. 2006; 40, 281-288.

2. Glaser, J.A.; Foerst, D.L.; McKee, G.D.; Quave, S.A.; Budde, W.L. Trace Analyses for Wastewaters. *Environ. Sci. Technol.* 1981**;** 15, 1426-1435.

## 17.0 Tables, Diagrams, Forms, Flowcharts, and Validation Data

This section contains all the method, tables, figures, diagrams, example forms for data recording, and flowcharts. This section will also contain validation data referenced in the body of the method.