

Guidance for the Selection of Analytical Methods and for the Evaluation of MDLs and PQLs

List Referenced in Chapter 62-4.246(4), F.A.C.

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For the List of Analytical Methods Referenced in Chapter 62-4.246(4), F.A.C.

Intended Use of This Document

This guidance is published to assist DEP staff and other data reviewers with the evaluation of appropriate analytical methodology used to generate data.

The 62-4.246(4) list referenced in this document provides **target** Method Detection Limits (MDLs) and Practical Quantitation Limits (PQLs) for a selected group of published analytical methods that may be used for the analysis of wastewater, surface water and groundwater.

Data reviewers can use the listed MDLs and PQLs as *guidelines* to ensure that adequately sensitive analytical techniques were utilized to meet permit requirements or other data quality objectives.

The target MDLs and PQLs in the 62-4.246(4) list may not be applicable to all samples.

Sources of Listed Target MDLs

The listed target MDLs are obtained from the following sources:

- 1) *MDLs published in official methods.* The EPA and APHA methods are the primary sources used.
- 2) *MDLs published in the Environmental Monitoring Methods Index (EMMI) and the National Environmental Monitoring Index (NEMI).*

MDLs from the sources above may differ for the same analyte-technique combination. In these cases, the MDL included in the 62-4.246(4) list was judged to be the most appropriate target value for the listed method.

Calculation of PQLs

- 1) *Listed PQLs were calculated as 4 X MDL, except as noted below.*
- 2) *PQLs are listed as equivalent to the MDL or as some other factor of the MDL for the following analytes, where the detection or quantitation value is affected by practical considerations associated with the analytical technique or, where the concept of a statistically derived MDL may not be appropriate:*

Biochemical Oxygen Demand (BOD)
Carbonaceous Biochemical Oxygen Demand (CBOD)

Chlorophyll
Coliforms, Fecal and Total
Color (selected methods)
Dioxin
Dissolved Oxygen (DO)
Enterococci
Hardness (by calculation)
Hydrogen ion (pH)
Hydrogen sulfide
Odor
Radiochemistry analytes
Residues (TDS, TSS)
Specific conductance
Temperature
Turbidity
Un-ionized ammonia

Reported Versus Target MDLs and PQLs

The listed MDLs and PQLs are targets that should be achievable ***under optimal conditions of quality control*** by most environmental laboratories. However, the laboratory cannot always be expected to meet the MDLs or PQLs listed in the table. Often, environmental samples will contain constituents that cause analytical interferences. Analytical interferences or other quality control problems can prevent achieving the target limits. Even sample collection anomalies (e.g., the collection of less than ideal sample volumes) can affect the MDL or PQL reported by the laboratory. Laboratory representatives should be able to explain the rationale behind the MDLs and PQLs reported with the analytical results, *especially if the reported MDLs and PQLs are above the required compliance limits*. If necessary, data reviewers should request documentation that demonstrates how the reported MDLs and PQLs were derived or adjusted.

Some laboratories may employ allowable modifications or optimizations of approved analytical methods that provide MDLs and PQLs lower than those found in the 62-4.246(4) list.

Reporting Data Below the MDL or PQL

Chapter 62-160, F.A.C., addresses reporting requirements for data submitted to the FDEP programs. Laboratory analytical reports should present the sample data in accordance with these requirements. Additionally, *data reporting instructions specific to DEP-required forms must be followed for regulatory compliance.*

“Non-detect” results

Whenever an analyte is not detected *at or above* the MDL, the MDL for the measurement must be reported along with the qualifier code “U” indicating that the analyte was not detected at the reported detection limit.

Results reported below the MDL

Alternately, laboratories have the option of reporting the analytical value from the sample analysis followed by the qualifier code “T” indicating the reported value was below the MDL.

Results below the PQL

If an analyte was detected *at or above* the MDL but was below the PQL, the result may be reported in one of two ways:

- 1) the value from the sample analysis can be reported with the qualifier code “I” , indicating that the analyte was detected but could not be quantified with certainty.
- 2) the PQL associated with the sample analysis can be reported followed by the qualifier code “M” indicating that the analyte was detected but was below the reported PQL.

Refer to Chapter 62-160, F.A.C. for a complete list of appropriate data qualifier codes.

If the analyte is not detected *at or above* the MDL or is detected at a level below the PQL, the reviewer should compare the reported MDL and PQL with the 62-4.246(4) list to determine if an appropriately sensitive method was utilized for the permit or other project objective. If the target MDL or PQL was not achieved, there may be valid reasons why this occurred and the reviewer should refer to justification provided by the laboratory.

MDLs and PQLs for “Calculated” Quantities

The following analytes are not tested by direct analysis but are calculated from the results of other analyses:

Hardness (by calculation)
Hydrogen sulfide
Nitrate (by calculation)
Un-ionized ammonia

MDLs and PQLs for the above calculated results are therefore not directly determinable. Limits reported for these analytical quantities are dependent on the limits for the component analyses and the number of significant figures carried in the calculations. The “MDLs” and “PQLs” in the 62-4.246(4) list for these calculated analytes were selected based on the above considerations.

Laboratory Certification Requirements

Laboratories must be certified by the DOH Environmental Laboratory Certification Program (ELCP) for all reported matrix-analyte-method combinations. Per 62-160, FAC, DEP may temporarily waive this requirement while the laboratory pursues certification with the DOH ELCP. Regardless of certification status, the laboratory shall operate under the effective NELAC standards.

Revisions to Analytical Methods

All citations of analytical methods in the 62-4.246(4) list refer to the edition of the method listed in 40 CFR Part 136.3. If the method is not listed in this federal rule, the most current, published edition of the method should be used.

Letter suffixes associated with EPA SW-846 method revisions have been omitted from the applicable entries in the 62-4.246(4) method list. The most current, published edition of the SW-846 method should be used.

Use of Additional Methods in 40 CFR Part 136.3 Not Found in the 62-4.246(4) Method List

Laboratories may use additional analytical methods approved at 40 CFR part 136.3 but not found in the 62-4.246(4) list.

The alternative method must be at least as sensitive as the MDL and PQL for the equivalent analytical technique listed in the 62-4.246(4) list, if applicable.

Use of Methods Not Found in 40 CFR Part 136.3

If no analytical method is listed in 40 CFR Part 136.3 for the analyte, the laboratory may use any method specified for the analyte in the 62-4.246 list, any applicable DEP rule or as approved by the applicable DEP regulatory program.

In some instances, approval for use of these alternative methods may be required by EPA and approval must be obtained prior to analyzing samples for NPDES permits.

The alternative method must be at least as sensitive as the MDL and PQL for the equivalent analytical technique listed in the 62-4.246(4) list, if applicable.

Analysis of Samples for Gross Alpha Activity with High Total Dissolved Solids (TDS)

The co-precipitation methods for gross alpha analysis found in the 62-4.246 list may be used instead of 40 CFR Part 136.3 methods for high-TDS samples where the sample matrix is otherwise expected to raise the MDL.

Reporting Total Chlorinated Phenols

For purposes of compliance with 62-302, FAC, *total chlorinated phenols* comprise the following:

- 4- Chloro-2-methylphenol
- 4- Chloro-3-methylphenol (4-chloro-*m*-cresol)
- 2- Chloro-5-methylphenol
- 3- Chlorophenol
- 4- Chlorophenol
- 2,3- Dichlorophenol
- 2,5- Dichlorophenol
- 2,6- Dichlorophenol
- 3,4- Dichlorophenol

- 3,5- Dichlorophenol
- 2,3,4,5- Tetrachlorophenol
- 2,3,4,6- Tetrachlorophenol
- 2,3,5,6- Tetrachlorophenol
- 2,3,4- Trichlorophenol
- 2,3,5- Trichlorophenol
- 2,3,6- Trichlorophenol
- 2,4,5- Trichlorophenol

Reporting Total Nitrogen

For purposes of compliance with any regulatory reporting requirements, *total nitrogen* is defined as the sum of the results of the sample analysis for total Kjeldahl nitrogen (TKN), nitrate (NO₃) and nitrite (NO₂). All concentrations should be reported as nitrogen (N) in mg/L.

List Of Acronyms And Abbreviations For Analytical Techniques

The following definitions apply to the analytical technique descriptions found in the 62-4.246(4) list.

A-GPC	Gas Flow Proportional Counter
AMP	Amperometric
A-SCINT	Scintillation Counter
Auto	Automated Analyzer
BAC-MF	Membrane Filter Technique
BAC-MPN	Most Probable Number (Multiple Tube Fermentation)
CALC	Calculated by Indirect Analysis
Chelation-FLAAS	Flame Atomic Absorption Spectroscopy with Sample Chelation Preparation
COLOR	Colorimetric
COND	Conductivity
CO-PRECIP	Co-precipitation Sample Preparation
COUL	Coulometric Titration
CVAAS	Cold Vapor Atomic Absorption Spectroscopy
DIFFUSION-Auto	Gas Diffusion – Automated Analyzer
FID	Flame Ionization Detector
FLAAS	Flame Atomic Absorption Spectroscopy
FLAAS-HYDRIDE	Flame Atomic Absorption Spectroscopy with Sample Hydride Preparation
FLUOR	Flourescence Spectrophotometry
GAS-FLOW-P	Gas Flow Proportional Counter
GC	Gas Chromatography
GC-ECD	Gas Chromatography - Electron Capture Detector
GC-ELCD	Gas Chromatography - Electrolytic Conductivity Detector
GC-ELCD-MCTD	Gas Chromatography- Electrolytic Conductivity or Microcoulometric Detector
GC-ELCD-PID	Electrolytic Conductivity and Photoionization Detector

GC-FID	Gas Chromatography-Flame Ionization Detector
GC-MS	Gas Chromatography-Mass Spectrometry
GC-NPD	Gas Chromatography-Nitrogen-Phosphorus Detector
GC-PID	Gas Chromatography-Photoionization Detector
GFAAS	Graphite Furnace - Atomic Absorption Spectrophotometry
GM	General Chemistry Method
GRAV	Gravimetry
HPLC	High Performance Liquid Chromatography
HPLC-UV	High Performance Liquid Chromatography-Ultraviolet Detector
HPLC-UV-FLUOR	High Performance Liquid Chromatography-Ultraviolet or Fluorescence Detector
Hydride	Flame Atomic Absorption Spectroscopy with Sample Hydride Preparation
IC	Ion Chromatography
ICP	Inductively Coupled Argon Plasma Emission Spectrophotometry
ICP-AES	Inductively Coupled Argon Plasma Emission Spectrophotometry
ICP-MS	Inductively Coupled Argon Plasma Mass Spectrometry
IMS-FA	Immunomagnetic Separation-Immunofluorescent Assay
IR	Infrared Detector
IR-COUL	Infrared Detector or Coulometric Titration
IR-COUL-COND	Infrared Detector or Coulometric Titration or Conductivity Detector
IR-FID	Infrared Detector or Flame Ionization Detector
ISE	Ion-specific Electrode
ISE-Auto	Ion-specific Electrode-Automated
LC-ION	Ion Chromatography
LDO	Luminescence-Based Dissolved Oxygen Sensor
NESSLER	Nesslerization
POT	Potentiometry
SPEC	Spectrophotometry
SPEC-Auto	Spectrophotometry-Automated Analyzer
TEMP	Temperature
TITR	Titration
TITR-Auto	Titration-Automated Analyzer
TSGF	Thermally Stabilized Platform Graphite Furnace
TURBID	Turbidity
TURBID All	Turbidity
UV-VIS	Ultraviolet-Visible Detector
UV-VIS-Auto	Ultraviolet-Visible Detector-Automated Analyzer

List Of Acronyms For Organizations and Sources of Methods

The following definitions apply to the acronyms for organizations cited in the 62-4.246(4) list.

ANS	American National Standard
AOAC	Official Methods of Analysis of the Association of Official Analytical Chemists
ASTM	American Society for Testing and Materials
Bran Luebbe	Bran & Luebbe Analyzing Technologies, Inc. (Industrial Methods)
Brooks-Blanchard	"A Procedure for the Determination of ²²⁸ Ra", I.B. Brooks & R.L. Blanchard
CFR	Code of Federal Regulations (U.S.)
DEP	Florida Department of Environmental Protection
DOE	U.S. Dept. of Energy, Environmental Measurements Laboratory Procedures Manual
DOH	Florida Department of Health
EPA	United States Environmental Protection Agency
HACH	"Hach Handbook of Water Analysis", Hach Chemical Company
NCASI	National Council for Air and Stream Improvement, Inc.
OIA ALPKEM	OI Analytical/ALPKEM Corporation
OIC	Oceanography International Corporation
ORION	Orion Research, Inc. (Instruction Manual for 97-70 electrode)
SM	"Standard Methods for the Examination of Water and Wastewater" (APHA)
USGS	"Techniques of Water-Resources Investigation of the U.S. Geological Survey"

List Of Acronyms And Abbreviations For Analytes, Units and Miscellaneous Terms

The following definitions apply to the acronyms and abbreviations for miscellaneous terms found in the 62-4.246(4) list.

ADMI	American Dye Manufacturers' Institute Color Value
BHC	Hexachlorocyclohexanes
COD	Chemical Oxygen Demand
Col/100 mL	Colonies per 100 mL of sample
D (2,4-)	2,4-Dichlorophenoxyacetic acid
DDE	1,1-Dichloro-2,2-di(p-chlorophenyl)ethylene
DDT	4,4'-Dichlorodiphenyltrichloroethane
degree C	Degrees celsius
DEP-SOP	DEP Standard Operating Procedures for Field Activities (DEP-SOP-001/01, Rev. 2/1/04)
DEP-SOP (NH ₃)	"Calculation Of Un-Ionized Ammonia In Fresh Water" (DEP Chemistry Laboratory, 2/12/01)
FAC	Florida Administrative Code
mg/L	milligrams per liter
mL	milliliter(s)
MPN/100 mL	Most Probable Number per 100 mL
NTU	Nephelometric Turbidity Units
PCB	Polychlorinated biphenyl

pci/L	picocuries per liter
PCU	Platinum Cobalt Unit
pg/L	picograms per liter
SU	Standard Units
TCDD	Tetrachloro-dibenzo-p-dioxin
TDS	Total Dissolved Solids
TON	Threshold Odor Number
TP(2,4,5-)	2-(2,4,5-Trichlorophenoxy)propionic acid (<i>Silvex</i>)
TSS	Total Suspended Solids
µg/L	micrograms per liter
µmhos/cm	micromhos per centimeter; equivalent to microsiemens per centimeter (µS/cm)