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# Unregulated Contaminant Monitoring Regulation Analytical Methods and Quality Control Manual

# Foreword

This document provides guidance regarding sampling, analytical methods, and related quality control issues for the States, EPA offices, water systems, and analytical laboratories participating in the Unregulated Contaminant Monitoring Regulation (UCMR) Program. This document is written for the personnel at a water system, laboratory, or agency who will be responsible for UCMR Program planning, implementation, and oversight.

Under the Safe Drinking Water Act (SDWA) as amended in 1996, §1445(a)(2)(A), the Environmental Protection Agency (EPA) is to promulgate regulations for a monitoring program for unregulated contaminants by August 1999. In the past, unregulated contaminant monitoring has been performed according to the program described in CFR 141.40. The 1996 SDWA Amendments direct a substantially revised UCMR Program.

The revised UCMR Program has a new list of contaminants to monitor, changes the number of public water systems (PWSs) that must conduct monitoring, and changes the frequency and schedule for monitoring. Additional regulatory actions include cancellation of unregulated contaminant monitoring for small systems serving 10,000 or fewer people under the existing unregulated contaminant monitoring program begun in 1989. The data collected in the revised UCMR will be used to support the development of the Contaminant Candidate List (CCL), to support the Administrator's determination of whether to regulate a contaminant, and to support the development of future regulations. The revised monitoring program is one of the cornerstones of the sound science approach to future drinking water regulation that is an aim of the 1996 SDWA Amendments.

# Disclaimers

This guidance document is designed to implement national policy concerning the UCMR Program. The document does not, however, substitute for the SDWA or EPA's regulations nor is this document a regulation itself. Thus, it cannot impose legally-binding requirements on EPA, States, or the regulated community, and may not apply to a particular situation based upon the circumstances. EPA decision makers retain the discretion to adopt approaches on a case-by-case basis that differs from this guidance where appropriate. EPA may change this guidance in the future.

Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

# Acknowledgments

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# Section 1. Introduction

## 1.1 Background on the Unregulated Contaminant Monitoring Regulation (UCMR)

The requirement to monitor unregulated contaminants was established by the 1986 Amendments to the Safe Drinking Water Act (SDWA). Public water systems (PWSs) were required to report the monitoring results for up to 48 unregulated contaminants to the States or primacy agency under several regulations (40 CFR 141.40(e), (j), and (n)(11) and (12)). Systems with less than 150 service connections were exempt, provided those systems made their facilities available for the States to monitor. The rules require repeat monitoring every 5 years.

Under §1445(a)(2)(A) of the SDWA, as amended in 1996, the Environmental Protection Agency (EPA) is to promulgate regulations that will substantially revise the existing unregulated monitoring program. The revised Unregulated Contaminant Monitoring Regulation (UCMR) Program has a new list of contaminants, changes the PWSs that must conduct monitoring, and changes the frequency and schedule for monitoring.

The UCMR has been developed in coordination with the Contaminant Candidate List (CCL) and the National Drinking Water Contaminant Occurrence Database (NCOD). The UCMR and the CCL will operate on an evolving 5-year cycle to assess the impact of new drinking water contaminants. The data collected through the UCMR Program will be used to support the development of the subsequent CCL, to support the Administrator's determination of whether or not to regulate a contaminant, and to develop regulations. The revised monitoring program is part of a sound science approach to future drinking water regulation, which is an aim of the 1996 SDWA Amendments.

The revised UCMR includes new and emerging contaminants. The revised UCMR will also require fewer systems to conduct monitoring than is required in the existing unregulated contaminant monitoring program. Therefore, the quality of data collected is a very important issue for the success of the revised program. This document provides a brief overview of the revised UCMR and outlines the required analytical methods and quality control procedures that PWSs and participating laboratories must adhere to while implementing the Assessment Monitoring component of the UCMR.

Further detailed information about the revised UCMR Program can be found in the Preamble to the proposed regulation (64 FR 23398) and the final Rule (64 FR _____ ), as well as other supporting documents. These documents are available from the EPA Water Docket, (202) 260-3027, Docket Number W-98-02. General information can also be obtained from the EPA Safe Drinking Water Hotline, (800) 426-4791, or through the EPA Office of Ground Water and Drinking Water Internet Homepage at www.epa.gov/ogwdw.

## 1.2 The Unregulated Contaminant Monitoring Regulation

The UCMR is required by SDWA as amended in 1996. Under the 1996 Amendments, EPA is required to promulgate a new regulation for monitoring unregulated contaminants. The regulation must include: (1) a new list of contaminants, of which not more than 30 may be required for monitoring, (2) a frequency and schedule for monitoring as based on PWS size, source water type, and likelihood of finding contaminants; (4) monitoring of only a representative sample of PWSs

serving 10,000 or fewer people; and, (5) requirements for placement of the monitoring data in the NCOD (in accordance with §1445 (g) of SDWA). PWSs must monitor to provide the location, concentration, and related information regarding the occurrence of these contaminants in public drinking water. EPA will analyze the monitoring data to identify which contaminants occur nationally and at concentrations that may warrant regulation. EPA will determine which contaminants pose the greatest risks to human health and, if necessary, will set priorities for regulation of the contaminants. Conversely, EPA may remove contaminants from consideration for regulation if UCMR monitoring indicates that these contaminants are not detected at significant levels in drinking water. EPA was required to develop a list of contaminants, the UCMR (1999) List, and regulations for monitoring the contaminants by August 1999. This list will be revised every 5 years.

EPA used the CCL (1998) contaminants listed as occurrence priorities as the primary basis for selecting contaminants for the UCMR (1999) List. The CCL identifies contaminants of potential concern that may occur or are likely to occur in drinking water. In order to establish the CCL (1998), EPA convened a Work Group to develop the CCL based on the results of previous unregulated contaminant monitoring and information from other data sources. The CCL team worked from a compendium of 10 lists containing approximately 391 chemical contaminants. The lists used in this process were: 1991 Drinking Water Priority List; Health Advisories; Integrated Risk Information System; Non-Target Analytes in Public Water Supply Samples; Comprehensive Environmental Response, Compensation, and Liability Act Priority List; stakeholder responses; Toxic Release Inventory; pesticides identified by the EPA Office of Pesticide Programs; a list of contaminants identified by the Safe Drinking Water Hotline; and a list of contaminants suspected of causing endocrine disruption.

The National Drinking Water Advisory Council's Working Group on Contaminant Occurrence and Selection, formed under the Federal Advisory Committee Act, developed the criteria for the CCL to address a contaminant's potential risk to public health and frequency of contaminant occurrence. Criteria for selecting contaminants for the CCL focused on occurrence in water at levels of health concern or indications of occurrence (production and release, coupled with contaminant properties). Health effects concentrations were used to determine the significance of occurrence. The CCL (1998) contains 50 chemical contaminants and 10 microbiological contaminants.

In establishing the CCL (1998), EPA divided the contaminants into three priority categories: those contaminants requiring additional research; those which need additional occurrence data; and those which are priorities for consideration for rule-making. EPA published a draft of the 1998 Drinking Water Contaminant Candidate List in the October 6, 1997 *Federal Register* (62 FR 52193). Comments submitted in response to the draft CCL were reviewed and considered in creating the final CCL, which was published in the March 2, 1998 *Federal Register* (63 FR 10273).

For purposes of the UCMR, EPA initially used the CCL occurrence priorities list to identify contaminants that were of national concern. The UCMR (1999) List, as initially proposed, included 32 of the 34 contaminants listed as occurrence priorities on the CCL (1998). At the time of the publication of the proposed UCMR, perchlorate and RDX were excluded from the UCMR (1999) List because it was thought that their occurrence was only a localized issue. As more data became available and after many public comments were received supporting the inclusion of these compounds, both perchlorate and RDX, as well as lead-210 and polonium-210, were added to the UCMR (1999) List.

## 1.3 Contaminants on the UCMR (1999) List

Although only 32 contaminants (24 chemical and 8 microbiological contaminants) listed on the CCL as occurrence priorities were initially proposed for inclusion on the UCMR (1999) List, all 34 contaminants listed as occurrence priorities on the CCL (1998) were eventually included on the final UCMR (1999) List. Two additional contaminants, lead-210 and polonium-210, were not included on the CCL (1998), but have been found in drinking water and in shallow aquifers in Florida. Because radionuclides have potential wide occurrence and consequent health risks and in response to public comments, EPA added lead-210 and polonium-210 to the UCMR (1999) List. These 36 contaminants comprise the revised list of UCMR (1999) contaminants (Table 1.1). For each of these contaminants, EPA evaluated the availability of analytical methods published by EPA and voluntary consensus standard organizations such as American Society for Testing and Materials (ASTM), the Association of Official Analytical Chemists (AOAC) and the American Public Health Association (APHA). In addition, EPA prioritized analytical methods development activities for those chemical and microbiological contaminants that did not have suitable analytical methods currently available.

The revised UCMR Program consists of three distinct monitoring components based upon the availability of suitable analytical methods. The Assessment Monitoring component of the UCMR Program will monitor for UCMR (1999) List 1 contaminants; these are the UCMR contaminants for which analytical methods are currently available.[1] These are the only UCMR contaminants for which monitoring is currently required under the revised UCMR Program.

The other UCMR (1999) contaminants, those on List 2 and List 3, will require monitoring when suitable analytical methods are developed. The Screening Survey component of the UCMR Program will monitor for UCMR (1999) List 2 contaminants for which analytical methods are nearly developed, and which have uncertain potential for occurrence. The Pre-Screen Testing component of the UCMR Program will monitor for UCMR (1999) List 3 contaminants for which analytical methods are in the early stages of development, and which may have newly emerged as concerns.

**Table 1.1 UCMR (1999) Contaminants**

| Chemical Contaminants | | |
|---|---|---|
| ***List*** | ***Contaminant Name*** | ***Potential Environmental Source*** |
| 1 | 2,4-dinitrotoluene | Used in the production of isocyanate and explosives |
| 1 | 2,6-dinitrotoluene | Used as mixture with 2,4-DNT (similar uses) |
| 1 | Acetochlor | Herbicide used with cabbage, citrus, coffee, and corn crops |
| 1 | DCPA di-acid degradate | Degradation product of DCPA, an herbicide used on grasses and weeds with fruit and vegetable crops |

[1] The two exceptions to this are perchlorate and acetochlor, for which analytical methods are currently being finalized. It is anticipated that these methods will be available before monitoring is to begin in 2001.

| List | Contaminant Name | Potential Environmental Source |
|---|---|---|
| 1 | DCPA mono-acid degradate | Degradation product of DCPA, an herbicide used on grasses and weeds with fruit and vegetable crops |
| 1 | DDE | Degradation product of DDT, a general insecticide |
| 1 | EPTC (s-ethyl-dipropylthio-carbamate) | Herbicide used on annual grasses, weeds, with potatoes and corn |
| 1 | Molinate | Selective herbicide used with rice, controls watergrass |
| 1 | MTBE (methyl tertiary-butyl ether) | Octane enhancer in unleaded gasoline |
| 1 | Nitrobenzene | Used in the production of aniline, which is used to make dyes, herbicides, and drugs |
| 1 | Perchlorate | Oxygen additive in solid fuel propellant for rockets, missiles, and fireworks |
| 1 | Terbacil | Herbicide used with sugarcane, alfalfa, and some fruit, etc. |
| 2 | 1,2-diphenylhydrazine | Used in the production of benzidine and anti-inflammatory drugs |
| 2 | 2-methyl-phenol | Released in automobile and diesel exhaust, coal tar and petroleum refining, and wood pulping |
| 2 | 2,4-dichlorophenol | Chemical intermediate in herbicide production |
| 2 | 2,4-dinitrophenol | Released from mines, metal, and petroleum plants |
| 2 | 2,4,6-trichlorophenol | By-product of fossil fuel burning, used as bactericide and wood/glue preservative |
| 2 | Alachlor ESA | Degradation product of alachlor, an herbicide used with corn, bean, peanut, and soybean crops to control grasses and weeds |
| 2 | Diazinon | Insecticide used with rice, fruit, vineyards, and corn crops |
| 2 | Disulfoton | Insecticide used with cereal, cotton, tobacco, and potato crops |
| 2 | Diuron | Herbicide used on grasses in orchards and with wheat crops |
| 2 | Fonofos | Soil insecticide used on worms and centipedes |
| 2 | Linuron | Herbicide used with corn, soybean, cotton, and wheat crops |
| 2 | Polonium-210 | Part of the uranium decay series; naturally occurring |
| 2 | Prometon | Herbicide used on annual and perennial weeds and grasses |
| 2 | RDX | Used in explosives; ammunition plants |
| 2 | Terbufos | Insecticide used with corn, sugar beet, and grain sorghum crops |
| 3 | Lead-210 | Part of the uranium decay series; naturally occurring |

| *List* | *Contaminant Name* | *Potential Environmental Source* |
|---|---|---|
| **Microbiological Contaminants** | | |
| 2 | *Aeromonas hydrophila* | Present in all freshwater and brackish water |
| 3 | Adenoviruses | Fecal or hand to mouth transmission |
| 3 | Cyanobacteria (blue-green algae, other freshwater algae, and their toxins) | Bloom in surface water bodies; produce toxins |
| 3 | Caliciviruses | Contaminated food and water; raw shellfish |
| 3 | Coxsackieviruses | Fecal or hand to mouth transmission |
| 3 | Echoviruses | Fecal or hand to mouth transmission |
| 3 | *Helicobacter pylori* | Fecal or hand to mouth transmission |
| 3 | Microsporidia | Occur in rivers, ponds, lakes, and unfiltered water |

Note: UCMR (1999) List 1 contaminants require monitoring under the Assessment Monitoring component of the revised UCMR. EPA is conducting analytical methods development for UCMR (1999) List 2 and List 3 contaminants. For more information on the Assessment Monitoring, Screening Surveys, and Pre-Screen Testing components of the UCMR, the reader may refer to the proposed UCMR Preamble and Rule (64 FR 23398) or the final Rule (64 FR _____ ).

This Analytical Methods and Quality Control Manual provides guidance for sampling and analytical and quality control procedures only for the UCMR (1999) List 1 contaminants. However, this Manual does not include quality control (QC) requirements pertaining to analyses of acetochlor and perchlorate, as the analytical methods for these compounds have not yet been approved for UCMR monitoring. EPA is currently refining analytical methods for acetochlor and perchlorate, and will be proposing a new regulation specifying both the approved analytical methods for the analyses of these compounds and the related implementation of a laboratory approval system. When these regulations are finalized, EPA will issue a supplement to this Manual detailing any additional QC procedures that must be followed while monitoring for these compounds under the revised UCMR.

Analytical methods and quality control procedures for the UCMR (1999) List 2 and List 3 contaminants are not discussed in this Manual. When suitable analytical methods are developed and approved for these other contaminants, a supplement (or supplements) to this Manual will be issued. The supplement(s) will provide the analytical methods and quality control details for UCMR (1999) List 2 and List 3 contaminant monitoring. A more complete review of methods availability is summarized in the proposed UCMR Preamble and Rule (64 FR 23398) and the final Rule (64 FR _____ ), as well as the *Contaminant Selection, Methods, and Sampling: Technical Background Information for the UCMR.* (This background document and other UCMR supporting documents are available from the EPA Water Docket, (202) 260-3027, Docket Number W-98-02. General information can also be obtained from the EPA Safe Drinking Water Hotline, (800) 426-4791, or through the EPA Office of Ground Water and Drinking Water Internet Homepage at www.epa.gov/ogwdw.) For identification of terms used throughout this Manual, see Appendix A (for a list of abbreviations and acronyms) and Appendix B (for a list of definitions).

### 1.3.1 UCMR (1999) List 1 Contaminants

The UCMR (1999) List 1 contaminants and their corresponding required sampling locations, suitable EPA analytical methods, and other related analytical details are listed in Table 1.2. There are a total of 12 chemical contaminants on the UCMR (1999) List 1. With the exceptions of perchlorate and acetochlor, EPA has approved suitable laboratory analytical methods for these contaminants, and monitoring is to begin in 2001 under the Assessment Monitoring component of the UCMR Program. As mentioned above, EPA plans to approve analytical methods for perchlorate and acetochlor and possibly an additional analytical method for nitrobenzene shortly. These methods should be approved and ready for use before monitoring is to begin in 2001.

**Table 1.2 UCMR (1999) List 1 Contaminants**

| Contaminants | CAS # | Approved Analytical Methods | Minimum Reporting Level | Sampling Point |
|---|---|---|---|---|
| 2,4-Dinitrotoluene | 121-14-2 | EPA 525.2 | 2 μg/L [a] | EPTDS [b] |
| 2,6-Dinitrotoluene | 606-20-2 | EPA 525.2 | 2 μg/L [a] | EPTDS [b] |
| 4,4'-DDE | 72-55-9 | EPA 508, EPA 508.1, EPA 525.2, D5812.96, 990.06 | 0.8 μg/L [a] | EPTDS [b] |
| Acetochlor | 34256-82-1 | Reserved [c] | Reserved [c] | EPTDS [b] |
| DCPA mono-acid degradate | 887-54-7 | EPA 515.1, EPA 515.2, D5317-93, 992.32 | 1 μg/L [a] | EPTDS [b] |
| DCPA di-acid degradate | 2136-79-0 | EPA 515.1, EPA 515.2, D5317-93, 992.32 | 1 μg/L [a] | EPTDS [b] |
| EPTC | 759-94-4 | EPA 507, EPA 525.2, D5475-93, 991.07 | 1 μg/L [a] | EPTDS [b] |
| Molinate | 2212-67-1 | EPA 507, EPA 525.2, D5475-93, 991.07 | 0.9 μg/L [a] | EPTDS [b] |
| MTBE | 1634-04-4 | EPA 524.2, D5790.95, SM6210D, SM6200B | 5 μg/L [d] | EPTDS [b] |
| Nitrobenzene | 98-95-3 | EPA 524.2, D5790.95, SM6210D, SM6200B | 12 μg/L [d] | EPTDS [b] |
| Perchlorate | 1497-73-0 | Reserved [c] | Reserved [c] | EPTDS [b] |
| Terbacil | 5902-51-2 | EPA 507, EPA 525.2, D5475-93, 991.07 | 2 μg/L [a] | EPTDS [b] |

Note: EPA = EPA Methods, D = ASTM Methods, SM = APHA Standard Methods, 900 series = AOAC Methods. See Table 1.5 for the full reference for each analytical method.

[a] Minimum Reporting Level (MRL) determined by multiplying by 10 the least sensitive method's minimum detection limit (MDL=standard deviation times the Student's T value for 99% confidence level with n-1 degrees of freedom), or when available, multiplying by 5 the least sensitive method's estimated detection limit (EDL=concentration of compound yielding approximately a five to one signal to noise ratio or the calculated MDL, whichever is greater).

[b] Entry Point to the Distribution System. This sample collection location is located at the entry point, after treatment, that represents each non-emergency water source in routine use over the 12-month period of monitoring; sampling must occur at the EPTDS, unless the State has specified other sampling points that are used for compliance monitoring under 40 CFR 141.24(f)(1), (2) and (3). If monitoring at source (raw) water sampling points indicates detection of any of the contaminants on the UCMR (1999) monitoring list, then the system must change the location of its unregulated contaminant monitoring to the EPTDS.

[c] To be determined.

[d] MRL for VOCs determined by multiplying by 10 either the published MDL or 0.5 μg/L, whichever is greater. The MDL of 0.5 μg/L (0.0005 mg/L) was selected to conform to the VOC MDL requirements of 40 CFR 141.24(f)(17)(i)(E).

### 1.3.2 UCMR (1999) List 2 and List 3 Contaminants

Currently there are no suitable analytical methods for the UCMR (1999) List 2 and List 3 contaminants. Therefore, monitoring is not currently required for these contaminants, but will be required in the future as analytical methods are developed and finalized. Listed in Table 1.3 are the UCMR (1999) List 2 contaminants, and related sampling and analytical information. Note that the analytical methods referenced here are only anticipated and have not been finalized. Analytical method development should be completed in time for Screening Survey monitoring to be conducted in 2001 and 2003.

**Table 1.3 UCMR (1999) List 2 Contaminants**

| Contaminant | CAS # | Anticipated Analytical Methods | Minimum Reporting Level | Sampling Point |
|---|---|---|---|---|
| 1,2-diphenylhydrazine | 122-66-7 | EPA 525.2 [a] | Reserved [b] | EPTDS [c] |
| 2-methyl-phenol | 95-48-7 | SPE/GC/MS [d] | Reserved [b] | EPTDS [c] |
| 2,4-dichlorophenol | 120-83-2 | SPE/GC/MS [d] | Reserved [b] | EPTDS [c] |
| 2,4-dinitrophenol | 51-28-5 | SPE/GC/MS [d] | Reserved [b] | EPTDS [c] |
| 2,4,6-trichlorophenol | 88-06-2 | SPE/GC/MS [d] | Reserved [b] | EPTDS [c] |
| Alachlor ESA | NA [e] | Reserved [b] | Reserved [b] | EPTDS [c] |
| Diazinon | 333-41-5 | EPA 525.2 [f] | Reserved [b] | EPTDS [c] |
| Disulfoton | 298-04-4 | EPA 525.2 [f] | Reserved [b] | EPTDS [c] |
| Diuron | 330-54-1 | SPE/HPLC/UV [g] | Reserved [b] | EPTDS [c] |
| Fonofos | 944-22-9 | EPA 525.2 [a] | Reserved [b] | EPTDS [c] |

| Contaminant | CAS # | Anticipated Analytical Methods | Minimum Reporting Level | Sampling Point |
|---|---|---|---|---|
| Linuron | 330-55-2 | SPE/HPLC/UV [g] | Reserved [b] | EPTDS [c] |
| Polonium-210 | 13981-52-7 | Reserved [b] | Reserved [b] | Reserved [b] |
| Prometon | 1610-18-0 | EPA 525.2 [f] | Reserved [b] | EPTDS [c] |
| RDX | 121-82-4 | Reserved [b] | Reserved [b] | EPTDS [c] |
| Terbufos | 13071-79-9 | EPA 525.2 [f] | Reserved [b] | EPTDS [c] |
| *Aeromonas hydrophila* | NA [e] | Reserved [b] | Reserved [b] | Reserved [b] |

[a] Contaminant currently not listed as analyte in this method. Methods under current development in an attempt to add this contaminant to the scope of this method. See Table 1.5 for full method reference.
[b] To be determined.
[c] Entry Point to the Distribution System. This sample collection location is located at the entry point, after treatment, that represents each non-emergency water source in routine use over the twelve-month period of monitoring; sampling must occur at the EPTDS, unless the State has specified other sampling points that are used for compliance monitoring under 40 CFR 141.24(f)(1), (2), and (3). If monitoring at source (raw) water sampling points indicates detection of any of the contaminants on the UCMR (1999) monitoring list, then the system must change the location of its unregulated contaminant monitoring to the EPTDS.
[d] Methods development currently in progress to develop a solid phase extraction/gas chromatography/mass spectrometry (SPE/GC/MS) method for the determination of this compound.
[e] CAS number is Not Applicable.
[f] Contaminant listed to be analyzed with this method. However, adequate sample preservation for this contaminant is not provided by the procedures for this method. Preservation studies are currently being developed for suitable sample preservation for this contaminant.
[g] Methods development currently in progress to develop a solid phase extraction/high performance liquid chromatography/ultraviolet (SPE/HPLC/UV) method for the determination of this compound.

Listed in Table 1.4 are the UCMR (1999) List 3 contaminants and related sampling and analytical information. Completion of method(s) development is not expected prior to the Assessment Monitoring or Screening Survey components of the UCMR Program. Instead, UCMR (1999) List 3 contaminants will be monitored during the Pre-Screen Testing component of the UCMR Program, most likely to be conducted in 2004.

**Table 1.4 UCMR List 3 (1999) Contaminants**

| Contaminant | CAS # | Anticipated Analytical Method | Minimum Reporting Level | Anticipated Sampling Point |
|---|---|---|---|---|
| Lead-210 | 14255-04-0 | Reserved [a] | Reserved [a] | Reserved [a] |
| Adenoviruses | NA [b] | Reserved [a] | Reserved [a] | Reserved [a] |
| Caliciviruses | NA [b] | Reserved [a] | Reserved [a] | Reserved [a] |
| Coxsackieviruses | NA [b] | Reserved [a] | Reserved [a] | Reserved [a] |

| Contaminant | CAS # | Anticipated Analytical Method | Minimum Reporting Level | Anticipated Sampling Point |
|---|---|---|---|---|
| Cyanobacteria (blue green algae, other freshwater algae, and their toxins) | NA[b] | Reserved[a] | Reserved[a] | Reserved[a] |
| Echoviruses | NA[b] | Reserved[a] | Reserved[a] | Reserved[a] |
| *Helicobacter pylori* | NA[b] | Reserved[a] | Reserved[a] | Reserved[a] |
| Microsporidia | NA[b] | Reserved[a] | Reserved[a] | Reserved[a] |

[a] To be determined.
[b] CAS number is Not Applicable.

## 1.4 Analytical Methods for UCMR (1999) List 1 Contaminants

Table 1.5 includes the UCMR (1999) List 1 contaminants and related analytical methods that are required for monitoring under the Assessment Monitoring component of the revised UCMR. The purpose of the revised UCMR is to obtain contaminant occurrence data in support of future regulatory decisions. The data required for regulatory decision-making must be of high quality. Most analytical methods are subject to some degree of false-negative test results (not detecting an contaminant when it is present), false-positive test results (either incorrectly identifying or detecting a contaminant, or introducing a contaminant into a sample when it is not present), and errors in the accuracy and precision of quantitative results.

For the UCMR (1999) List 1 contaminants laboratory analyses, EPA has approved the use of alternative (i.e., non-EPA) analytical methods of the voluntary consensus standard organizations (including the ASTM, AOAC, and APHA). These methods are identified and listed with the equivalent EPA method in Table 1.5. Note, however, that whether EPA or one of the alternative methods are used, additional quality control measures for UCMR analyses are required. The additional quality control measures are included in the revised UCMR (40 CFR 141.40) and are explained in this Manual. In the following sections of this Manual, EPA method numbers are used as references for the reader.

The data quality needs of drinking water compliance monitoring data are different compared to the evaluation and use of occurrence data. The purpose of compliance monitoring is to determine whether or not a contaminant is present in the drinking water above the established Maximum Contaminant Level (MCL). Unless the concentration of the contaminant closely approaches the MCL, even imprecise data can be used to assure the data user that the contaminant is not present at a concentration above the MCL. In contrast, the usefulness of occurrence data is much more dependent on the precision of the measurement. The ability to perform valid and meaningful statistical analyses is directly dependent on the precision of the data when determining, for example, the percentage of U.S. waters which have contaminant X above the minimum reporting level (MRL) or if contaminant X occurs more frequently or at higher concentrations in one type of water or geographical region than in another.

The ability to correctly identify a chemical contaminant is directly related to the type of chemical and the analytical method used. For example, contaminants such as the disinfection by-products are far less likely to be misidentified than pesticides or herbicides, because disinfection by-products are typically present at relatively high concentrations in disinfected waters, while pesticides and herbicides are much less likely to be present, or are present at much lower concentrations. The analytical method selected will also determine the accuracy of the qualitative identification. In general, the most reliable qualitative identifications come from methods which use mass spectral data for contaminant identification. However, these methods are typically less sensitive than methods that rely on less selective detectors.

To ensure that the data collected under this regulation are of sufficient quality to meet the requirements of these regulatory decisions, EPA is specifying that only the analytical methods and procedures listed in Table 1.5 be used in obtaining these data. This Manual explains additional quality control requirements and contaminant confirmation procedures that are specified in the regulation. The subsequent sections of this Manual provide an overview of methods, sampling, and quality control procedures to be used in the UCMR Assessment Monitoring program. As methods are approved for perchlorate and acetochlor, EPA will issue a supplement to this Analytical Methods and Quality Control Manual. Furthermore, EPA will issue additional supplements to this Manual as new methods become available for the additional contaminants listed in Tables 1.3 and 1.4.

**Table 1.5 Approved Analytical Methods for UCMR (1999) List 1 Contaminants**

| Chemical Contaminant | CAS # | Methodology | |
|---|---|---|---|
| | | EPA Method | Equivalent Methods |
| **Volatile Organic Compounds** | | | |
| MTBE | 1634-04-4 | EPA 524.2 [a] | D5790-95 [b]; SM6210D [c]; SM6200B [c] |
| Nitrobenzene | 98-95-3 | EPA 524.2 [a, e] | D5790-95 [b]; SM6210D [c]; SM6200B [c] |
| **Semivolatile Organic Compounds** | | | |
| 2,4-Dinitrotoluene | 121-14-2 | EPA 525.2 [a] | none identified |
| 2,6-Dinitrotoluene | 606-20-2 | EPA 525.2 [a] | none identified |
| **Chlorinated Hydrocarbon Pesticides** | | | |
| DDE | 72-55-9 | EPA 525.2 [a]; EPA 508 [a]; EPA 508.1 [a] | D5812-96 [b]; 990.06 [d] |
| **Nitrogen- and Phosphorus-Containing Pesticides** | | | |
| EPTC | 759-94-4 | EPA 525.2 [a]; EPA 507 [a] | D5475-93 [b]; 991.07 [d] |
| Molinate | 2212-67-1 | EPA 525.2 [a]; EPA 507 [a] | D5475-93 [b]; 991.07 [d] |

| Chemical Contaminant | CAS # | Methodology | |
|---|---|---|---|
| | | EPA Method | Equivalent Methods |
| Terbacil | 5902-51-2 | EPA 525.2[a]; EPA 507[a] | D5475-93[b]; 991.07[d] |
| **Acid Herbicides** | | | |
| DCPA mono-acid degradate | 887-54-7 | EPA 515.1[a,f]; EPA 515.2[a,f] | D5317-93[b]; 992.32[d] |
| DCPA di-acid degradate | 2136-79-0 | EPA 515.1[a,f]; EPA 515.2[a,f] | D5317-93[b]; 992.32[d] |

[a] The version of the EPA methods which you must follow for this Rule are listed at 40 CFR 141.24 (e).

[b] *Annual Book of ASTM Standards,* 1996 and 1998, Vol. 11.02, American Society for Testing and Materials. Method D5812-96 is located in the *Annual Book of ASTM Standards*, 1998, Vol. 11.02. Methods D5790-95, D5475-93, and D5317-93 are located in the *Annual Book of ASTM Standards*, 1996 and 1998, Vol 11.02. Copies may be obtained from the American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

[c] SM 6200 B is only found in the 20th edition of *Standard Methods for the Examination of Water and Wastewater*, 1998. Sample preservation must be conducted as specified in EPA Method 524.2. SM 6210 D is only found in the 18th and 19th editions of *Standard Methods for the Examination of Water and Wastewater*, 1992 and 1995, American Public Health Association; either edition may be used. Copies may be obtained from the American Public Health Association, 1015 Fifteenth Street NW, Washington, DC 20005.

[d] *Official Methods of Analysis of AOAC* (Association of Official Analytical Chemist) International, Sixteenth Edition, 4th Revision, 1998, Volume I, AOAC International, First Union National Bank Lockbox, PO Box 75198, Baltimore, MD 21275-5198. (800) 379-2622.

[e] Specific recommendations regarding the use of EPA Method 524.2 for measuring nitrobenzene are included in Section 6 of this Manual. Note that EPA is currently conducting methods development research to determine if nitrobenzene is compatible with the preservation requirements of EPA Method 525.2. If research indicates that EPA Method 525.2 is suitable for monitoring nitrobenzene, EPA will issue a public notice and provide for a public comment period prior permitting the use of EPA Method 525.2 for measuring nitrobenzene.

[f] Additional recommendations for these methods are listed in Section 6 of this Manual.

# Section 2. Sampling Plan

## 2.1 Monitoring By Public Water Systems

The focus of the monitoring in the revised UCMR is on occurrence or likely occurrence of contaminants in the drinking water of community and non-transient, non-community water systems. For regulatory purposes, public water systems (PWSs) are categorized as "community water systems," or "non-community water systems". Community water systems (CWSs) are specifically defined as "public water systems which serve at least 15 service connections used by year-round residents or regularly serve at least 25 year-round residents," while a non-transient non-community water system (NTNCWS) means "a public water system that is not a community water system" (40CFR141.2). These non-community systems are available to serve the public, but do not do so on a year-round basis in most cases, or do so but are used by people on a temporary basis (e.g., used by people traveling).

PWSs will monitor at the sampling sites and at the sampling frequencies specified in the revised UCMR (40 CFR 141.40). EPA or the State will provide further specifications and guidance on the monitoring schedule and other requirements to the PWSs. The subsequent general discussion of sampling is for informational purposes only and does not alter the requirements specified in the regulation or in directions from the State or EPA to PWSs.

### 2.1.1 Systems Required To Monitor

Under this program, all CWSs and NTNCWSs serving more than 10,000 people (large systems) are required to monitor for unregulated contaminants. However, PWSs that purchase their water must only monitor for UCMR contaminants that must be sampled for in the distribution system (i.e., the sampling point is listed as "distribution line"). For systems serving 10,000 or fewer people (small systems), only a statistically selected, nationally representative sample of 800 CWSs and NTNCWSs must monitor. EPA will pay for the reasonable costs of monitoring for this representative sample of small systems. The State or EPA will notify those systems selected for inclusion in the national representative sample. Transient non-community water systems will not be included in this monitoring.

From the representative sample of 800 systems, EPA will select 20 to 30 systems to serve as "Index" systems. Information collected from these systems will provide a broader understanding of small systems. Index systems must monitor each year during the 5-year UCMR cycle. Data collected from Index systems will provide information on the effects of seasonal and annual variability, pumping cycles, and other environmental and program factors that may affect UCMR monitoring results. EPA will provide additional guidance and instructions to the Index systems. EPA will provide contractor support to collect and ship samples as well as gather additional Index system data.

## 2.2 Sampling Frequency

PWSs will conduct their Assessment Monitoring during 1 year of the Assessment Monitoring period 2001 to 2003 (except for the Index systems, which will monitor every year from 2001-2005, as discussed above). The year of monitoring and the time of sample collection should coincide, to the extent practical, with other scheduled compliance monitoring. For example, a low-vulnerability

system that may only monitor for compliance purposes during 1 year in a 3-year period could collect its required UCMR samples during that same year. Further, to the extent practical, analyses for the UCMR should be coordinated with analyses for other required monitoring using the same methods to help reduce costs.

PWSs using surface water sources, or ground water under the influence of surface water, must sample four times per year for 1 year during the Assessment Monitoring period. One of the sampling times must occur between May 1 and July 31, or another period of greatest vulnerability specified by the State or EPA. Large PWSs using surface water or ground water under the influence of surface water must select either the first, second, or third month of a quarter and sample in that same month of each of four consecutive quarters. In other words, systems must monitor under one of the following quarterly sampling schedules: January, April, July, October; or February, May, August, November; or March, June, September, December. PWSs using ground water sources will sample two times per year for 1 year during the Assessment Monitoring period, with one of these sampling times occurring between May 1 and July 31, or another period of greatest vulnerability as specified by the State or EPA. The second set of samples for ground water systems must be collected 5 to 7 months before or after the vulnerable period sampling event. For all small PWSs participating in the national representative sample of small systems, the State or EPA will specify the day, plus or minus 2 weeks, on which samples must be collected.

## 2.3 Sampling Points

Sampling must be performed at the locations specified in the UCMR Program. The required UCMR sampling locations, referred to as sampling points, are contaminant- specific and are summarized in Table 1.2 for the UCMR (1999) List 1 contaminants. Possible sampling points for the UCMR (1999) List 2 and List 3 contaminants are listed in Tables 1.3 and 1.4, respectively.

For contaminants on the UCMR (1999) List 1, samples must be collected at entry points to the distribution system (EPTDSs) representing each non-emergency water source in routine use over the 12-month period of monitoring, unless the State has specified other sampling points that are used for compliance monitoring under 40 CFR 141.24(f)(1), (2), and (3). Thus UCMR samples may be collected from either the EPTDS or from the source (raw) water if the State has specified that source water sampling points are to be used for standard compliance monitoring. However, if monitoring at source water sampling points indicates detection of any of the contaminants on the monitoring list, then the system must shift its unregulated contaminant monitoring to the EPTDS for all future monitoring under the UCMR, unless the State or EPA determines that no treatment or processing was in place that would affect the measurement of the contaminants. In that case, the additional sampling at the EPTDS would not be required. The requirement for UCMR samples to be collected at the EPTDS follows the existing regulatory approach and provides data for exposure assessment.

# Section 3. Sample Collection and Preservation

## 3.1 Chemical Contaminants

Sample preservation and holding times for the contaminant-specific analytical determinative methods specified in the UCMR Program are summarized in Table 3.1. The sample collection and preservation procedures described below must be followed for all samples collected for the UCMR. If these procedures are not followed, the Rule specifies that resampling is required within 14 days of the observance of the error.

### 3.1.1 Nitrogen- and Phosphorus-Containing Pesticides

The three UCMR (1999) List 1 nitrogen- and phosphorus-containing pesticides, EPTC[2], molinate[2], and terbacil[2], may be analyzed with EPA Method 525.2, EPA Method 507 or the approved equivalent methods including ASTM Method D5475-93 or AOAC Method 991.07 (see Table 1.5). For reference, see EPA Method 507 - *Determination of Nitrogen- and Phosphorus-Containing Pesticides in Water by Gas Chromatography with a Nitrogen-Phosphorus Detector* (Table 1.5). (Sampling procedures based on EPA Method 525.2 are described below in Section 3.1.5). Sample procedures based on EPA Method 507, including sample containers, chlorine testing and dechlorination, and sample collection, preservation, storage, and holding times are described below:

**Sample container** - Use one-liter or one-quart amber glass bottles fitted with Teflon-lined screw caps. Amber bottles are required for the UCMR to protect samples from light. The bottle must be washed and dried as described in Section 4.1.1 of the EPA Method before use to minimize contamination. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736 or equivalent) and extracted with methanol overnight prior to use.

**Residual chlorine determination** - If water to be sampled is known or suspected to contain residual chlorine, determination of the level of residual chlorine is necessary. Diethyl-p-phenylenediamine (DPD) test-kits are commercially available and can be used to determine the level of residual chlorine in the field. Determine and record the level of residual chlorine in the water to be sampled. If the water to be sampled contains residual levels of chlorine, each sample will need to be dechlorinated.

**Sample dechlorination** - To dechlorinate the sample, add approximately 80 milligrams of sodium thiosulfate per liter of sample to the sample containers prior to filling. If needed, add as much additional sodium thiosulfate as necessary to eliminate all residual chlorine.

**Sample collection** - When sampling from a water tap, remove any aeration equipment, open the tap and allow the system to flush until the water temperature has stabilized, usually about two minutes. Collect the sample directly from a tap and not through any plastic or rubber hoses or tubing. Adjust the flow to a slow but steady stream (about the diameter of a pencil) and collect samples from the flowing stream. When using automatic samplers, use refrigerated glass sample containers if possible. Sampling equipment, including automatic samplers, must be free of plastic tubing, gaskets, and other parts that may leach interfering analytes into the water sample.

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2 These pesticides are also semi-volatile organic compounds and therefore are also discussed in Section 3.1.5

Fill the sample bottles until almost full, but take care not to flush out any dechlorination chemicals from the sample bottle. After the sample bottle has been filled, close the bottle, invert three or four times, and keep the sample bottle sealed until analysis.

The method specifies the addition of the biocide mercuric chloride to the sample to retard microbiological degradation. Mercuric chloride, however, is being withdrawn because it is highly toxic and poses handling and disposal problems. Mercuric chloride should not, therefore, be used to preserve samples for the UCMR Program.

**Sample storage** - Immediately store the samples at 4°C (±2°) . To do so, place the samples on ice or with frozen cold packs in a cooler, or place in a refrigerator that can maintain the samples at 4°C (±2°). Keep the samples at 4°C (±2°) from the time of collection until extraction.

**Sample holding time** - Extract samples within 14 days. Preservation study results indicated that most method contaminants present in samples were stable for 14 days when stored under these conditions. The contaminants EPTC and terbacil exhibited recoveries of less than 60% after 14 days; consequently, the maximum sample holding time for these contaminants is 14 days. If samples are not extracted within this period, discard and replace the samples.

**Sample extract storage and holding time** - Analyze extracts within 14 days. Store extracts at 4°C (±2°) away from light. Preservation study results indicate that most contaminants are stable for 28 days; however, a 14-day maximum extract storage time is recommended. (See Table 3.1 for a summary of holding times.) If samples are not analyzed within the appropriate period, discard and replace the samples.

### 3.1.2 Chlorinated Hydrocarbon Pesticides

The UCMR (1999) List 1 chlorinated hydrocarbon pesticide, 4,4'-DDE[3], may be analyzed with EPA Method 508, 508.1, 525.2 or the approved equivalent methods, including ASTM Method D5812-96 and AOAC Method 990.06 (see Table 1.5). Sampling procedures based on EPA Method 525.2, including sample containers, chlorine testing and dechlorination, and sample collection, preservation, storage, and holding times are described below in Section 3.1.5. Sampling procedures based on EPA Methods 508 and 508.1 are described below:

EPA Method 508 - *Determination of Chlorinated Pesticides in Water by GC with an Electron Capture Detector* (see Table 1.5).

**Sample container** - Use one-liter Amber glass bottles fitted with Teflon-lined screw caps. Amber bottles are required for the UCMR to protect samples from light. The container must be washed and dried before use as described in Section 4.1.1 of the EPA Method to minimize contamination. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736) and extracted with methanol overnight prior to use.

**Residual chlorine determination** - If water to be sampled is known or suspected to contain residual chlorine, determination of the level of residual chlorine is necessary. Diethyl-p-phenylenediamine

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[3] The pesticide 4,4'-DDE is a semi-volatile organic compound and is therefore also discussed in Section 3.1.5.

(DPD) test-kits are commercially available and can be used to determine the level of residual chlorine in the field. Determine and record the level of residual chlorine in the water to be sampled. If the water to be sampled contains residual levels of chlorine, each sample will need to be dechlorinated.

**Sample dechlorination** - To dechlorinate the sample, add approximately 80 milligrams of sodium thiosulfate per liter of sample to the sample containers prior to filling. If needed, add as much additional sodium thiosulfate as necessary to eliminate all residual chlorine.

**Sample collection** - When sampling from a water tap, remove any aeration equipment, open the tap and allow the system to flush until the water temperature has stabilized, usually about two minutes. Collect the sample directly from a tap and not through any plastic or rubber hoses or tubing. Adjust the flow to a slow but steady stream (about the diameter of a pencil) and collect samples from the flowing stream. When using automatic samplers, use refrigerated glass sample containers, if possible. Sampling equipment, including automatic samplers, must not contain plastic tubing, gaskets, and other similar parts or materials that may leach chemicals into the sample.

Fill the sample bottles until almost full, but take care not to flush out any dechlorination chemicals from the sample bottle. After the sample has been collected, close the bottle, invert three or four times, and keep the sample sealed from collection time until analysis.

The method specifies the addition of the biocide mercuric chloride to the sample to retard microbiological degradation. Mercuric chloride, however, is being withdrawn because it is highly toxic and poses handling and disposal problems. Mercuric chloride should not, therefore, be used to preserve samples for the UCMR Program.

**Sample storage** - Immediately store the samples at 4°C (± 2°). To do so, place the samples on ice or with frozen cold packs in a cooler, or place in a refrigerator that can maintain the samples at 4°C (± 2°). Keep the samples at 4°C (± 2°) from the time of collection until analysis.

**Sample holding time** - Preservation study results indicate that most of the target contaminants present in the samples are stable for 7 days when stored under these conditions. Contaminant stability may be affected by the matrix; therefore, the analyst should verify that the preservation technique is applicable to the samples under study. (See Table 3.1 for a summary of holding times.) If samples are not extracted within the appropriate period, discard and replace the samples.

**Sample extract storage and holding time** - Store sample extracts at 4°C (±2°), away from light. A 14-day maximum extract storage time is recommended. However, contaminant stability may be affected by the matrix; therefore, the analyst should verify appropriate extract holding times applicable to the samples under study. If samples are not analyzed within the appropriate period, discard and replace the samples.

EPA Method 508.1 - *Determination of Chlorinated Pesticides, Herbicides, and Organohalides by Liquid-Solid Extraction and Electron Capture Gas Chromatography* (see Table 1.5).

**Sample container** - Use one-liter or one-quart amber glass bottles fitted with Teflon-lined screw caps. Amber bottles are required for the UCMR because some of the method contaminants are sensitive to light and are oxidized or decomposed upon exposure to light.

**Residual chlorine determination** - If water to be sampled is known or suspected to contain residual chlorine, determination of the level of residual chlorine is necessary. Diethyl-p-phenylenediamine (DPD) test-kits are commercially available and can be used to determine the level of residual chlorine in the field. Determine and record the level of residual chlorine in the water to be sampled. If the water to be sampled contains residual levels of chlorine, each sample will need to be dechlorinated.

**Sample dechlorination** - To dechlorinate the sample, add approximately 80 milligrams of sodium sulfite per liter of sample to the sample containers prior to filling. If needed, add as much additional sodium sulfite as necessary to eliminate all residual chlorine.

**Sample collection** - When sampling from a water tap, remove any aeration equipment, open the tap and allow the system to flush until the water temperature has stabilized, usually about two minutes. Collect the sample directly from a tap and not through any plastic or rubber hoses or tubing. Adjust the flow to a slow but steady stream (about the diameter of a pencil) and collect samples from the flowing stream. When using automatic samplers, use refrigerated glass sample containers if possible. Sampling equipment, including automatic samplers, must be free of plastic tubing, gaskets, and other parts that may leach interfering analytes into the water sample.

Fill the sample bottles until almost full, but take care not to flush out any dechlorination chemicals from the sample bottle. After collecting the sample, close the bottle, invert three or four times, and wait one minute until preserving the sample with acid.

**Sample preservation** - The one minute waiting period after sample collection is crucial; it is important to reduce the level of residual chlorine before preserving the sample with acid. If the acid is added immediately following collection, the dechlorination reaction may be incomplete. This allows residual free chlorine to oxidize and/or chlorinate PAHs in the sample, including the surrogate standard specified by the method. Also, do *not* directly mix hydrochloric acid and sodium sulfite prior to sampling.

After waiting one minute, adjust the pH to less than 2 by carefully adding 6 N hydrochloric acid (this may require as much as 4 milliliters of acid). This should retard the microbiological degradation of the contaminants in water. Also, this is the same pH used in the extraction, and is required to support the recovery of acidic compounds. Close the sample bottle, Teflon face down, invert three or four times, and keep the sample sealed until analysis.

**Sample storage** - Samples must be iced or refrigerated at 4°C (±2°) from the time of collection until extraction. Immediately store the samples at 4°C (±2°). To do so, place the samples on ice or with frozen cold packs in a cooler, or place in a refrigerator that can maintain the samples at 4°C (±2°). Keep the samples at 4°C (±2°) from the time of collection until analysis.

**Sample holding time** - Extract samples within 14 days. Preservation study results show that the UCMR contaminants are stable for 14 days in samples that are preserved as described in Sections 8.2 and 8.3 of the EPA Method. (See Table 3.1 for a summary of holding times.) If samples are not extracted within this period, discard and replace the samples.

**Sample extract holding time** - Analyze sample extracts within 30 days (refrigerated sample extracts may be stored up to 30 days prior to analysis). If sample extracts are not analyzed within this period, discard and replace the samples.

### 3.1.3 Acid Herbicides

The two UCMR (1999) List 1 acid herbicide-based contaminants, the mono- and di-acid degradates of dimethyl tetrachloro terephthalate (DCPA), may be analyzed with EPA Method 515.1, EPA Method 515.2 or the approved equivalent methods including ASTM Method D5319-93 and AOAC Method 992.32 (see Table 1.5). For reference, see EPA Method 515.1 - *Determination of Chlorinated Acids in Water by Gas Chromatography with an Electron Capture Detector* or EPA Method 515.2 - *Determination of Chlorinated Acids in Water Using Liquid-Solid Extraction and Gas Chromatography with an Electron Capture Detector* (Table 1.5). It is important to note that because the approved methods do not allow for the identification and quantification of the individual acids, the single analytical result obtained should be reported as total DCPA mono- and di-acid degradates. For specific clarifications concerning the use of EPA Methods 515.1 and 515.2 or their approved equivalent methods, please see Section 6.1 of this Manual. Sampling procedures based on EPA Methods 515.1 and 515.2, including sample containers, chlorine testing and dechlorination, and sample collection, preservation, storage and holding times are described below:

**Sample container** - If samples are being collected for EPA Method 515.1 or an approved equivalent method, use one-liter or one-quart amber glass bottles fitted with Teflon-lined screw caps. If samples are being collected for EPA Method 515.2 or an approved equivalent method, use 250 milliliter amber glass bottles fitted with Teflon-lined screw caps. Amber bottles are being required to protect samples from light. The container must be washed and dried as described in Section 4.1.1 of the EPA Methods before use to minimize contamination. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736) and extracted with methanol overnight prior to use.

**Residual chlorine determination** - If water to be sampled is known or suspected to contain residual chlorine, determination of the level of residual chlorine is necessary. Diethyl-p-phenylenediamine (DPD) test-kits are commercially available and can be used to determine the level of residual chlorine in the field. Determine and record the level of residual chlorine in the water to be sampled. If the water to be sampled contains residual levels of chlorine, each sample will need to be dechlorinated.

**Sample dechlorination** - To dechlorinate the sample, add approximately 80 milligrams of sodium thiosulfate per liter of sample to the sample container prior to filling. If needed, add as much additional sodium thiosulfate as necessary to eliminate all residual chlorine.

**Sample collection** - When sampling from a water tap, remove any aeration equipment, open the tap and allow the system to flush until the water temperature has stabilized, usually about two minutes. Collect the sample directly from a tap and not through any plastic or rubber hoses or tubing. Adjust the flow to a slow but steady stream (about the diameter of a pencil) and collect samples from the flowing stream. When using automatic samplers, use refrigerated glass sample containers if possible. Sampling equipment, including automatic samplers, must be free of plastic tubing, gaskets, and other parts that may leach interfering analytes into the water sample.

Fill the sample bottles until almost full, but take care not to flush out any dechlorination chemicals from the sample bottle. After collecting the sample, close the sample bottle, invert three or four times, and keep the sample bottle sealed until analysis.

The method specifies the addition of the biocide mercuric chloride to the sample to retard microbiological degradation. Mercuric chloride, however, is being withdrawn because it is highly

toxic and poses handling and disposal problems. Mercuric chloride should not, therefore, be used to preserve samples for the UCMR Program.

Sample preservation procedures in EPA Method 515.2 are similar to those listed in EPA Method 515.1, with the exception samples collected for EPA Method 515.2 must be acidified via the addition of 6 N HCl. If samples are being collected for EPA Method 515.2, be sure to wait one minute after dechlorinating the sample before preserving it with acid to ensure that the dechlorination reaction is complete.

**Sample storage** - Immediately store the samples at 4°C (±2°) . To do so, place the samples on ice or with frozen cold packs in a cooler, or place in a refrigerator that can maintain the samples at 4°C (±2°). Keep the samples at 4°C (±2°) from the time of collection until extraction.

**Sample holding time** - Extract samples within 14 days. However, contaminant stability will very likely be affected by the matrix; therefore, the analyst should verify that the preservation technique is applicable to the samples under study. Preservation study results from EPA Method 515.1 indicate that the contaminants (measured as total acid) present in samples are stable for 14 days when stored under these conditions. Preservation study results for EPA Method 515.2 indicate that the sample contaminants (measured as total acid) are stable in water for 14 days when stored under these conditions. If samples are not extracted within the appropriate period, discard and replace the samples.

**Sample extract storage and holding time** - Store extracts at 4°C (±2°) away from light. Analyze extracts within 28 days, according to EPA Method 515.1 and 14 days according to EPA Method 515.2. However, the analyst should verify that appropriate extract holding times are applicable to the samples under study. Preservation study results indicate that most contaminants are stable for 28 days according to EPA Method 515.1 and 14 days according to EPA Method 515.2. (See Table 3.1 for a summary of holding times.) If samples are not extracted within the appropriate period, discard and replace the samples.

### 3.1.4 Volatile Organic Compounds

The two UCMR (1999) List 1 volatile organic compounds (VOCs) monitored under the revised UCMR Program, methyl tertiary-butyl ether (MTBE) and nitrobenzene, may be analyzed with EPA Method 524.2 or an approved equivalent method, such as ASTM Method D5790-95 or APHA (Standard Methods) SM6210D or SM6200B (see Table 1.5). For reference, see EPA Method 524.2 - *Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry,* or an approved equivalent method. It is important to keep the sample bottles in an area known to be free of VOCs prior to sample collection. General sampling procedures based on EPA Method 524.2, including sample containers, chlorine testing, dechlorination, sample collection, sample preservation, storage and holding times, are described below. For specific analytical method recommendations pertaining to the use of EPA Method 524.2 for measuring nitrobenzene, please see Section 6.2 of this Manual. The sampling requirements detailed in EPA Method 524.2 must also be followed when using any of the approved equivalent methods.

**Sample containers** - Use 40-milliliter to 120-milliliter screw cap glass vials, each equipped with a Teflon-faced silicon septum. To prepare sample bottles: wash vials and septa with detergent and

rinse with distilled water; air dry the vials and septa at room temperature; place in a 105°C oven for one hour; then remove and allow to cool in an area known to be free of organics.

**Residual chlorine determination** - If water to be sampled is known or suspected to contain residual chlorine, determination of the level of residual chlorine is necessary. Diethyl-p-phenylenediamine (DPD) test-kits are commercially available and can be used to determine the level of residual chlorine in the field. Determine and record the level of residual chlorine in the water to be sampled. If the water to be sampled contains residual levels of chlorine, each sample will need to be dechlorinated.

**Sample dechlorination** - To dechlorinate the sample, add approximately 25 milligrams ascorbic acid (or 3 milligrams sodium thiosulfate[4]) per 40 milliliter of sample volume to sample container prior to collecting the sample. If necessary to eliminate all residual chlorine, add an additional 25 milligrams ascorbic acid (or 3 milligrams sodium thiosulfate) per each 5 milligrams per liter residual chlorine in the sample.

**Sample collection** - Collect all samples in duplicate or triplicate. When sampling from a water tap, remove any aeration equipment, open the tap and allow the system to flush until the water temperature has stabilized, usually about two minutes. Collect the sample directly from a tap and not through any plastic or rubber hoses or tubing. Adjust the flow from the tap to a slow but steady stream (about the diameter of a pencil) and collect the sample from the flowing stream. When using automatic samplers, use refrigerated glass sample containers, if possible. Sampling equipment, including automatic samplers, must not contain plastic tubing, gaskets, and other similar parts or materials that may leach chemicals into the sample.

Fill sample to almost overflowing, but take care not to flush out any dechlorination chemicals that are in the sample bottle. Do not let air bubbles pass through the sample as the sample bottle is filled, and, when sealed, the sample bottle must contain no air bubbles. After the sample bottle has been filled, close the bottle and invert three or four times, and then wait one minute before preserving the sample with acid.

**Sample preservation** - The one-minute waiting period after sample collection is crucial; it is important to reduce the residual chlorine before preserving the sample with acid. If the acid is added immediately following sample collection, the dechlorination reaction may be incomplete.

After one minute, adjust the pH to less than 2 by carefully adding two drops of 1:1 hydrochloric acid for every 40 milliliters of sample. (The hydrochloric acid preservation reduces sample pH in order to retard microbiological degradation of the contaminants being analyzed.) Ensure that no air bubbles are trapped in the completely full sample bottle. Close the sample bottle, Teflon face down, and invert three or four times. Keep the sample bottle sealed from collection time until analysis.

**Sample storage** - Immediately store the samples at 4°C (± 2°). To do so, place the samples on ice or with frozen cold packs in a cooler, or place in a refrigerator that can maintain the samples at 4°C (± 2°). Keep the samples at 4°C (± 2°) from the time of collection until analysis. The sample storage area must be free of organic solvent vapors, excess heat and direct light.

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[4] Because neither MTBE nor nitrobenzene boil below 25°C, sodium thiosulfate may be used to reduce residual chlorine.

**Sample holding time** - Analyze all samples within 14 days of collection (see Table 3.1 for a summary of holding times). If samples are not analyzed within this period, discard and replace the samples.

### 3.1.5 Semi-volatile Organic Compounds

The six[5] UCMR (1999) List 1 semi-volatile organic compounds, 2,4-dinitrotoluene, 2,6-dinitrotoluene, 4,4'- DDE[6], s-ethyl-dipropylthiocarbamate (EPTC)[7], molinate[7], and terbacil[7], may be analyzed with EPA Method 525.2 or the approved equivalent methods including ASTM Methods D5812-96 and D5475-93, or AOAC Methods 990.06 or 991.07. Note that two of these semi-volatile organic compounds (2,4-dinitrotoluene and 2,6-dinitrotoluene) can be analyzed with only the EPA approved analytical method; there are no approved equivalent methods for these two contaminants. See Table 1.5 for a listing of the approved equivalent analytical methods for each contaminant. For reference, see EPA Method 525.2 - *Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry*, or an approved equivalent method. General sampling procedures based on EPA Method 525.2, including sample containers, chlorine testing and dechlorination, and sample collection, preservation, storage, and holding times, are described below:

**Sample containers** - Use one-liter or one-quart amber glass bottles fitted with Teflon-lined screw caps. Amber bottles are required for the UCMR because some of the method contaminants are very sensitive to light and are oxidized or decomposed upon exposure to light. It is important to keep the sample bottles in an area known to be free of volatile and semi-volatile organic compounds prior to sample collection.

**Residual chlorine determination** - If water to be sampled is known or suspected to contain residual chlorine, determination of the level of residual chlorine is necessary. Diethyl-p-phenylenediamine (DPD) test-kits are commercially available and can be used to determine the level of residual chlorine in the field. Determine and record the level of residual chlorine in the water to be sampled. If the water to be sampled contains residual levels of chlorine, each sample will need to be dechlorinated.

**Sample dechlorination** - To dechlorinate the sample, add approximately 40-50 milligrams of sodium sulfite to sample container prior to collecting the sample. If needed, add as much sodium sulfite as necessary to eliminate all residual chlorine.

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5 It is anticipated that acetochlor and possibly nitrobenzene will be added to the scope of this method once further methods development research has been completed. If EPA Method 525.2 and the equivalent voluntary consensus standards are approved for measuring acetochlor and nitrobenzene, a supplement to this Manual will be issued.

6 This semi-volatile organic compound is a pesticide and is specifically identified and listed as a chlorinated pesticide in Table 1.5.

7 These three semi-volatile organic compounds are pesticides and are specifically identified and listed as nitrogen/phosphorus pesticides in Table 1.5.

**Sample collection** - When sampling from a water tap, remove any aeration equipment, open the tap and allow the system to flush until the water temperature has stabilized, usually about two minutes. Collect the sample directly from a tap and not through any plastic or rubber hoses or tubing. Adjust the flow from the tap to a slow but steady stream (about the diameter of a pencil) and collect the sample from the flowing stream. When using automatic samplers, use refrigerated glass sample containers, if possible. Sampling equipment, including automatic samplers, must not contain plastic tubing, gaskets, and other similar parts or materials that may leach chemicals into the sample.

Fill sample to almost overflowing, but take care not to flush out any dechlorination chemicals that are in the sample bottle. After the sample bottle has been filled, close the bottle and invert three or four times, and then wait one minute before preserving the sample with acid.

**Sample preservation** - The one-minute waiting period after sample collection is crucial to reduce the level of residual chlorine before preserving the sample with acid. If the acid is added immediately following collection, the dechlorination reaction may be incomplete. This allows residual free chlorine to oxidize and/or chlorinate poly-aromatic hydrocarbons (PAHs) in the sample (as noted in Section 13.2.1 of the Method) including the internal and surrogate standards specified by the method. Because of the degradation/oxidation of the internal standards, calculated results based on internal standard recovery can be erroneously elevated. Also, do *not* directly mix hydrochloric acid and sodium sulfite prior to sampling.

After waiting one minute, adjust the pH to less than 2 by carefully adding 6 N hydrochloric acid (this may require as much as 4 milliliters of acid). This should retard the microbiological degradation of the contaminants in water. Also, this is the same pH used in the extraction, and is required to support the recovery of acidic compounds. Close the sample bottle, Teflon face down, invert three or four times, and keep the sample sealed until analysis.

**Sample storage** - Immediately store the samples at 4°C (± 2°). To do so, place the samples on ice or with frozen cold packs in a cooler, or place in a refrigerator that can maintain the samples at 4°C (± 2°). Keep the samples at 4°C (± 2°) from the time of collection until analysis. Sample storage area must be free of organic contaminants, excess heat, and direct light.

**Sample holding time** - Extract the samples within 14 days of sample collection and analyze the extracts within 30 days of sample collection. Results of the holding time and storage study of all method contaminants showed that most are stable for 14 days in water samples when the samples are dechlorinated, preserved, and stored as described above. (See Table 3.1 for a summary of holding times.) If samples are not analyzed within this period, discard and replace the samples.

**Table 3.1 Preservation and Holding Times for Approved Analytical Methods**

| Method(s) | Preservation | Sample Holding Time | Extract Holding Time | Sample Size | Container |
|---|---|---|---|---|---|
| EPA 507<br>D5475-93<br>991.07 | Sodium thiosulfate;<br>Cool 4°C; Dark | 14 days | 14 days<br>(4°C, Dark) | 1 L | Amber Glass with Teflon-lined Cap |
| EPA 508<br>D5812-96<br>990.06 | Sodium thiosulfate;<br>Cool 4°C; Dark | 7 days | 14 days<br>(4°C, Dark) | 1 L | Amber Glass with Teflon-lined Cap |
| EPA 508.1<br>D5812-96<br>990.06 | Sodium sulfite;<br>6 N HCl - pH < 2;<br>Cool 4°C | 14 days | 30 days | 1 L | Amber Glass with Teflon-lined Cap |
| EPA 515.1<br>D5317-93<br>992.32 | Sodium thiosulfate;<br>Cool 4°C; Dark | 14 days | 28 days<br>(4°C, Dark) | 1 L | Amber Glass with Teflon-lined Cap |
| EPA 515.2<br>D5317-93<br>992.32 | Sodium thiosulfate;<br>6 N HCl - pH < 2;<br>Cool 4°C; Dark | 14 days | 14 days<br>(4°C, Dark) | 250 mL | Amber Glass with Teflon-lined Cap |
| EPA 524.2<br>D5790-95<br>SM6210D<br>SM6200B | Ascorbic acid or Sodium thiosulfate;<br>1:1 HCl - pH < 2;<br>Cool 4°C | 14 days | N/A | 40 - 120 mL | Glass with Teflon-lined Septum |
| EPA 525.2 | Sodium sulfite;<br>6 N HCl - pH < 2;<br>Cool 4°C; Dark | 14 days | 30 days from collection | 1 L | Amber glass with Teflon-lined Cap |

Note: EPA = EPA Methods, D = ASTM Methods, SM = APHA Standard Methods, 900 series = AOAC Methods. See Table 1.5 for the full reference for each analytical method.

## 3.2 Monitoring of Routine Water Quality Parameters

In addition to the requirement that systems monitor for UCMR contaminants, the revised UCMR also specifies that certain chemical and physical parameters must be measured in the field at each sampling point from which UCMR samples are collected. These parameters are being required because they are important indicators of water quality and may contribute to the likelihood of the contaminants being found in drinking water. EPA believes that these parameters will allow for a more thorough scientific understanding of the occurrence of unregulated contaminants. As all UCMR (1999) List 1 contaminants are chemicals, EPA is only requiring that the pH of the water being sampled is measured and reported. For UCMR (1999) List 2 and List 3 contaminants, some of which are microbiological in nature, monitoring of additional water quality parameters such as

temperature, total disinfectant residual, etc., may be required. The analytical methods approved for measuring pH are included in Table 3.2 below.

**Table 3.2 Water Quality Parameters to be Monitored with UCMR (1999) List 1 Contaminants**

| Parameter | Contaminant Type | Methodology | | |
|---|---|---|---|---|
| | | EPA Method | Standard Methods | Other |
| pH | Chemical | 150.1 [a]<br>150.2 [a] | 4500-$H^+$ B [b] | ASTM D1293-84 [c]<br>ASTM D1293-95 [c] |

[a] Methods 150.1 and 150.2 are available from US EPA, NERL, 26 W. Martin Luther King Dr., Cincinnati, Ohio 45268. The identical methods are also in "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, March 1983, available from the National Technical Information Service (NTIS), U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, Virginia 22161, PB84-128677. The NTIS toll-free number is (800) 553-6847.

[b] The 18th and 19th Editions of *Standard Methods for the Examination of Water and Wastewater*, 1992 and 1995. Method 4500-$H^+$ B can also be found in the 20th Edition *Standard Methods for the Examination of Water and Wastewater*, 1998, American Public Health Association, 1015 Fifteenth St. NW, Washington, DC, 20005.

[c] *Annual Book of ASTM Standards*, Editions 1994 and 1996,Volumes 11.01, American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA 19428. Version D1293-84 is located in the *Annual Book of ASTM Standards*,1994, Volumes 11.01. Version D1293-95 is located in the *Annual Book of ASTM Standards*, 1996, Volumes 11.01.

# Section 4. Sample Transport

Immediately after sample collection place all UCMR samples on ice or with frozen cold packs in an insulated container, cooler, or place in a refrigerator to cool the samples to 4°C (±2°). Keep the samples at 4°C (±2°) from the time of collection until analysis, including during any necessary transport. Do not let any samples freeze. If transporting samples to an off-site laboratory, pack samples in insulated containers or coolers carefully to protect against sample bottle breakage during transport. Samples are commonly transported to off-site laboratories via laboratory pick-up service, delivery by the water system's own personnel, or delivery with a commercial courier service.

Transport the appropriately cooled [i.e., 4°C (±2°)] and packed samples to the analytical laboratory as soon as possible after sample collection. Transporting the samples within 2 days of sample collection is strongly recommended; transporting the samples immediately—the same day of sample collection—is advised. Note that samples must be packed with sufficient ice or frozen cold packs to ensure that samples are maintained at 4°C (± 2°) during the entire transport period, but do not let any samples freeze. All samples must be processed by the laboratory within 7 to 14 days of sample collection; therefore, provide adequate time for sample pick-up, transport, delivery, extraction, and analysis. Immediate (sample collection day) transport of samples to the laboratory will ensure adequate sample analysis time and will greatly reduce the chance that systems will need to re-collect samples due to late samples exceeding holding times.

# Section 5. UCMR Quality Control Requirements

Several quality control (QC) methods required for UCMR monitoring by EPA are methods currently required and in use under other SDWA regulations. As a result, mechanisms for reviewing laboratory qualifications are already in place for determination of other chemical contaminants determined by these methods. Laboratories that provide data to the EPA in support of the UCMR must document that they are currently approved by a State and that they have State certification and/or approval to perform those analyses using UCMR-specified methods. Additionally, laboratories must also complete and document initial demonstration of capability for all contaminants requiring monitoring by UCMR-specified methods.

UCMR Assessment Monitoring must be conducted only using the analytical methods specified in the UCMR (see Table 1.5). The QC procedures specified in these approved analytical methods as well as additional QC procedures identified in this Manual must be followed to ensure accurate and precise data.

QC procedures and the frequency of QC testing vary among the methods. Many of the methods specified in the UCMR provide criteria to be used in evaluating and accepting laboratory performance based on related QC data. This section describes the various QC procedures EPA requires as part of the UCMR and the rationale for acceptance criteria. Because EPA cannot accept monitoring data if the applicable QC requirements are not met, laboratories must strictly adhere to the QC described in this section. The following will cause monitoring data to be excluded from the database:

- failure to use the correct calibration check standard concentration
- failure to verify the calibration curve at the specified frequency
- failure to meet the acceptance criteria for verifying calibration
- contaminants detected in the laboratory reagent (method) blank at concentrations equal to or more than one-half the minimum reporting level (MRL)
- when applicable, failure to meet the acceptance criteria for the internal standard
- when applicable, failure to meet the acceptance criteria for the surrogate standard
- failure to analyze samples and/or extracts within the specified holding times

Certain QC data must also be reported as part of the analytical services performed for the UCMR. These data are being collected to evaluate the quality of the monitoring data. These reporting requirements are noted in the reporting elements in Section 7 of this Manual.

## 5.1 Minimum Reporting Level

The minimum reporting level (MRL) concentrations listed in Table 5.1 were determined by multiplying by 10 the least sensitive method's minimum detection limit (MDL),[8] or, when available, multiplying by 5 the least sensitive method's estimated detection limit (EDL).[9] The MRL for VOCs was determined by multiplying by 10 either the published MDL or 0.5 micrograms per liter, whichever is greater. The MDL of 0.5 micrograms per liter (0.0005 milligrams per liter) was selected to conform to the VOC MDL requirements of 40 CFR 141.24(f)(17)(i)(E).

**Table 5.1 UCMR Methods and Minimum Reporting Levels**

| Contaminant | Approved UCMR Analytical Methods | Minimum Reporting Level |
|---|---|---|
| 2,4-Dinitrotoluene | EPA 525.2 | 2 μg/L [a] |
| 2,6-Dinitrotoluene | EPA 525.2 | 2 μg/L [a] |
| 4,4'-DDE | EPA 508; EPA 508.1; EPA 525.2; D5812.96; 990.06 | 0.8 μg/L [a] |
| Acetochlor | Reserved [b] | Reserved [b] |
| DCPA mono- and di-acid degradates . | EPA 515.1; EPA 515.2; D5317-93; 992.32 | 1 μg/L [a] |
| EPTC | EPA 507; EPA 525.2; D5475-93; 991.07 | 1 μg/L [a] |
| Molinate | EPA 507; EPA 525.2; D5475-93; 991.07 | 0.9 μg/L [a] |
| MTBE | EPA 524.2; D5790.95; SM6210D; SM6200B | 5 μg/L [c] |
| Nitrobenzene | EPA 524.2; D5790.95; SM6210D; SM6200B | 12 μg/L [c] |
| Perchlorate | Reserved [b] | Reserved [b] |
| Terbacil | EPA 507; EPA 525.2; D5475-93; 991.07 | 2 μg/L [a] |

Note: EPA = EPA Methods, D = ASTM Methods, SM = APHA Standard Methods, 900 series = AOAC Methods. See Table 1.5 for the full reference for each analytical method.

[a] Minimum reporting level (MRL) determined by multiplying by 10 the least sensitive method's minimum detection limit (MDL = standard deviation times the Student's t value for 99% confidence level with n-1 degrees of freedom), or when available, multiplying by 5 the least sensitive method's estimated detection limit (EDL=concentration of compound yielding approximately a five to one signal to noise ratio or the calculated MDL, whichever is greater).

[b] To be determined.

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8 The MDL equals the standard deviation times the Student's t value for 99% confidence level with n-1 degrees of freedom.

9 The EDL equals the concentration of compound yielding approximately a five to one signal to noise ratio or the calculated MDL, whichever is greater.

[c] MRL for VOCs determined by multiplying by 10 either the published MDL or 0.5 μg/L, whichever is greater. The MDL of 0.5 μg/L (0.0005 mg/L) was selected to conform to the VOC MDL requirements of 40 CFR 141.24(f)(17)(i)(E).

Laboratories must demonstrate that they can achieve reliable data at the MRL for each contaminant. Therefore, the calibration curve must encompass the MRL concentration. The laboratory must verify the accuracy of the curve at the MRL by analyzing a calibration check standard at the MRL concentration (see Section 5.2 of this Manual).

EPA recognizes that some laboratories are able to provide reliable data at concentrations lower than those shown in Table 5.1. To achieve consistency in the National Drinking Water Contaminant Occurrence Database (NCOD), laboratories are only required to report quantitative results for concentrations equal to or greater than the MRLs. However, EPA also recognizes the usefulness of receiving more complete results to allow evaluation of the analytical method implementation. Systems and laboratory that are able to reliably report results below the MRL are encouraged to do so. To report reliable results obtained below the MRL, laboratories and/or water systems should do three things:

1) For data element 6, Analytical Results - Sign, report a "<," indicating that the result obtained is less than the MRL listed in Table 5.1.

2) For data element 7, Analytical Result - Value, report the actual concentration value obtained for the contaminant.

3) For data element 17, Presence/Absence, report the contaminant as "Present."

The combination of these three steps will allow for the reporting of data below the MRL, and will enable EPA to more fully evaluate the MRL for the respective contaminant and assist in determining what the final MRL might be if EPA requires future monitoring of the contaminant.

## 5.2 Calibration

Each method describes calibration procedures that are used to determine the concentrations of the method contaminants. Some methods allow several options:

- a calibration curve based on either external standards or detector responses to the contaminant relative to an internal standard
- an average response factor for each contaminant

The laboratory must select and follow one of the calibration procedures outlined in the approved method to meet the requirements of the UCMR. In addition, the mass spectral (MS) methods, EPA Methods 524.2 and 525.2, have specific tuning criteria that must be met prior to performing the calibration procedure.

All methods specified in the UCMR require that calibration span the expected concentration range of the samples being analyzed. The number of calibration standards necessary to meet this

requirement varies from three to six, depending on the method. The UCMR does not require laboratories to change method calibration procedures with the exception that the low level standard must be at or below the MRL specified for each contaminant, and the mid-level standard must simply be near the midpoint of the calibration range.

### 5.2.1 Calibration Verification

Complete calibration curves are not required on a daily basis. However, the analyst must periodically verify calibration during sample analysis to ensure accuracy of the analytical results. The frequency at which calibration must be checked varies according to the analytical method used. Frequency requirements for verifying calibration have been established by EPA to meet the accuracy requirements for the UCMR and are presented in Table 5.2.

Most of the methods recommend checking the instrument calibration using a mid-level calibration check standard. The method acceptance criteria for verifying calibration are based on this standard. However, to meet the objectives of the UCMR, calibration must be verified across the range of contaminant concentrations that are being measured. Based on the recommendations from technical experts experienced with these methods, EPA is specifying calibration verification at low- and mid-levels for each method.

The frequency of verifying calibration for UCMR samples is based on the number of samples analyzed together in an analysis batch. For Assessment Monitoring, an analysis batch is defined as samples analyzed using the same instrument within a 24-hour period. However, the maximum number of UCMR samples that can be included in one analysis batch is 30. The 24-hour period begins with the analysis of the low-level calibration check standard and it ends with the analysis of the final calibration check standard. The 24-hour period does not necessarily include the analysis time used to generate the calibration curve. However, if a new curve is prepared each time samples are analyzed, the 24-hour period still begins with the analysis of the low-level calibration check standard.

When determining the 30 sample maximum, do not count method blanks, shipping blanks, initial and continuing calibration check standards, matrix spikes (MSs), matrix spike duplicates (MSDs), and any independent QC samples that are analyzed with the UCMR samples.

Analysis of the low-level calibration check standard must be completed prior to analysis of any samples; each contaminant must meet the acceptance criteria provided in Table 5.3. If the criteria cannot be met, identify and eliminate the source of the problem, then perform a new instrument calibration according to the method calibration procedures.

It is important to note that an acceptable end calibration check standard must be analyzed before analyses of other samples (i.e., non-UCMR samples) may begin. Thus, if the last five samples analyzed were part of the UCMR, the analyst must perform an acceptable end calibration check standard before starting non-UCMR analyses.

For all methods, after analyses of no more than 10 UCMR samples, the calibration curve must be verified using either a low- or mid-level continuing calibration check standard; each contaminant must meet the acceptance criteria listed in Table 5.3 or 5.4. If the criteria are not met, reanalyze all samples or extracts that were analyzed between this standard and the last standard meeting

acceptance criteria for the problem contaminant(s) after the calibration problem is resolved. If the samples or extracts cannot be re-analyzed, then the data for the problem contaminant(s) are considered invalid for those samples and should not be reported to EPA.

**Table 5.2 Frequency Requirements for Verifying Calibration**

| Methods | Method Specifications | UCMR Specifications | |
|---|---|---|---|
| | | Initial | Continuing |
| EPA 507<br>D5475-93<br>991.07 | each working day | each batch of 30 samples or daily (whichever is more frequent) | alternate between low- and mid-level standard after every 10 samples |
| EPA 508<br>D5812-96<br>990.06 | each working day | | |
| EPA 508.1<br>D5812-96<br>992.32 | each 12 hour shift | | |
| EPA 515.1<br>D5317-93<br>992.32 | each working day | | |
| EPA 515.2<br>D5317-93<br>992.32 | each working shift | | |
| EPA 524.2<br>D5790-95<br>SM6210D<br>SM6200B | every 12 hours | | |
| EPA 525.2 | every 12 hours | | |

Note: EPA = EPA Methods, D = ASTM Methods, SM = APHA Standard Methods, 900 series = AOAC Methods. See Table 1.5 for the full reference for each analytical method.

**Table 5.3 UCMR Low-Level Calibration Check Standard Concentrations and Acceptance Criteria**

| Contaminant | MRL (µg/L) | Concentration of Low-Level Standard | Acceptance Criteria |
|---|---|---|---|
| 2,4-dinitrotoluene | 2 µg/L | ≤ MRL | ± 40 % |
| 2,6-dinitrotoluene | 2 µg/L | ≤ MRL | ± 40 % |
| 4,4'-DDE | 0.8 µg/L | ≤ MRL | ± 40 % |

| Contaminant | MRL (µg/L) | Concentration of Low-Level Standard | Acceptance Criteria |
|---|---|---|---|
| Acetochlor | Reserved[a] | Reserved[a] | Reserved[a] |
| DCPA mono- and di-acid degradates | 1 µg/L | ≤ MRL | ± 40 % |
| EPTC | 1 µg/L | ≤ MRL | ± 40 % |
| Molinate | 0.9 µg/L | ≤ MRL | ± 40 % |
| MTBE | 5 µg/L | ≤ MRL | ± 40 % |
| Nitrobenzene | 12 µg/L | ≤ MRL | ± 40 % |
| Perchlorate | Reserved[a] | Reserved[a] | Reserved[a] |
| Terbacil | 2 µg/L | ≤ MRL | ± 40 % |

[a] To be determined.

**Table 5.4 Mid-Level Calibration Check Standard Concentrations and Acceptance Criteria**

| Contaminant | Mid-Level Standard | Acceptance Criteria |
|---|---|---|
| 2,4-dinitrotoluene | middle of calibration range | ± 20 % |
| 2,6-dinitrotoluene | middle of calibration range | ± 20 % |
| 4,4'-DDE | middle of calibration range | ± 20 % |
| Acetochlor | Reserved[a] | Reserved[a] |
| DCPA mono- and di-acid degradates | middle of calibration range | ± 20 % |
| EPTC | middle of calibration range | ± 20 % |
| Molinate | middle of calibration range | ± 20 % |
| MTBE | middle of calibration range | ± 20 % |
| Nitrobenzene | middle of calibration range | ± 20 % |
| Perchlorate | Reserved[a] | Reserved[a] |
| Terbacil | middle of calibration range | ± 20 % |

[a] To be determined.

## 5.3 Method Detection Limit

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the contaminant concentration is greater than zero. Usually, measurements at the MDL concentration are considered qualitative, because they are not precise enough to meet the needs of the data user. If accurate and precise data are required, do not report below the level at which the necessary precision and accuracy are achieved.

Laboratories must calculate their MDLs for each analysis (using the primary column) according to the procedure in CFR §136 Appendix B (included in this Manual as Appendix C), with the following additional requirements:

- Include all sample processing steps in the determination. Conduct extractions and analyses over at least 3 days.
- Select a spiking concentration which is less than or equal to the established MRL for each contaminant monitored by the UCMR. Analyze a total of seven duplicates of reagent water spiked at a concentration less than or equal to the established MRL as listed in Table 5.1. From the data collected from these analyses, calculate measurement accuracy. Each data point must be within ±50% of the value of the spiked solution concentration.
- Calculate the MDL for each contaminant according to the formula listed in CFR §136 Appendix B (included in this Manual as Appendix C). **Do not subtract the blank value as suggested in the procedure.**
- To ensure the accuracy of data reported for the UCMR, laboratory calculated MDL levels for each contaminant must be less than or equal to one-half of the MRL listed in Table 5.1.

## 5.4 Laboratory Reagent (Method) Blank

All of the methods approved for the UCMR require periodic analysis of a laboratory reagent (method) blank. For all methods, a method blank is defined as 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 other samples. This blank is used to determine if method contaminants or other interferences are present in the laboratory environment, the reagents, or the apparatus.

The frequency of the method blank analysis depends on the type of sample manipulation required prior to the instrumental analysis. Methods that involve extraction of the sample usually stipulate analysis of a method blank with each set of samples that are extracted together. When the samples are analyzed directly, a blank is analyzed on a daily basis.

The required frequencies for analyzing method blanks for the UCMR are listed in Table 5.5. To meet the objectives of the UCMR, analyze the method blank as the first sample on the instrument (immediately following the initial calibration check standard). For methods that involve extractions, carry the method blank through the extraction process. **Each extraction batch of samples must include a method blank.**

An extraction batch is defined as all samples prepared/extracted together by the same person(s) during a work day (normally an 8-10 hour period for routine working schedules). Use the same lot of extracting solvent, internal standard spiking solution, and surrogate standard spiking solution for all samples included in a batch. When applicable, derivatize all samples in an extraction batch with the same batch of derivatizing agent. Include a maximum of 20 UCMR samples in an extraction batch. When determining the 20 sample maximum, do not count method blanks, shipping blanks, calibration check standards, any independent QC samples, duplicate samples, and spiked samples that are extracted with UCMR samples.

While some methods state that background interferences should be below the MDL, the general goal for all methods approved for the UCMR is to ensure that the background levels are low enough to not interfere with an accurate measurement. If any of the method analytes are detected at a concentration equal to or greater than one-half the MRLs (see Table 5.6), then perform no further analyses until the source of the problem is identified and eliminated. If the source is traced to any material that was used in the preparation of the set of samples to be analyzed, then discard all these prepared samples (or extracts) and repeat the preparation procedure using another aliquot of each sample. If the samples cannot be re-extracted, then consider all data for the problem contaminant(s) invalid for all samples in the extraction or analysis batch, as appropriate, and flag the monitoring data as not meeting QC criteria. Data not meeting UCMR QC criteria should not be reported to EPA.

Contamination problems in the extraction process cannot be detected until the analysis step. If a problem is discovered, then the data for one or more contaminants in all the samples in the extraction batch are lost unless the laboratory has a back-up aliquot of each sample which can be extracted. EPA limited the extraction batch to 20 UCMR samples to minimize the number of samples that could be potentially lost because of a contamination problem. More than one batch of samples may be extracted within a day.

Laboratories should be aware of the potential for carry-over between samples when highly contaminated samples are analyzed. To avoid this, laboratories may find that additional blanks are needed to "rinse" the system after high concentration samples are analyzed. If blanks are analyzed for this purpose, the laboratory is not required to report data from these analyses.

**Table 5.5 Frequency Requirements for Analyzing Laboratory Reagent (Method) Blanks**

| Method | Method Specifications | UCMR Specifications |
|---|---|---|
| EPA 507<br>D5475-93<br>991.07 | 1 per sample set or if reagents changed | 1 per sample batch (≤20 samples) |
| EPA 508<br>D5812-96<br>990.06 | 1 per sample set or if reagents changed | 1 per sample batch (≤20 samples) |
| EPA 508.1<br>D5812-96<br>992.32 | 1 per sample set per 12 hour shift | 1 per sample batch (≤20 samples) |

| Method | Method Specifications | UCMR Specifications |
|---|---|---|
| EPA 515.1<br>D5317-93<br>992.32 | 1 per sample set | 1 per sample batch (≤20 samples) |
| EPA 515.2<br>D5317-93<br>992.32 | 1 per sample set | 1 per sample batch (≤20 samples) |
| EPA 524.2<br>D5790-95<br>SM6210D<br>SM6200B | each batch or 1 per 20 samples | 1 per sample batch (≤20 samples) |
| EPA 525.2 | every 12 hour extraction batch | 1 per sample batch (≤20 samples) |

Note: EPA = EPA Methods, D = ASTM Methods, SM = APHA Standard Methods, 900 series = AOAC Methods. See Table 1.5 for the full reference for each analytical method.

**Table 5.6 UCMR Acceptance Criteria for Laboratory Reagent (Method) Blanks**

| Contaminant | Minimum Reporting Level | Maximum Allowable Background Concentration (≤ ½ MRL) |
|---|---|---|
| 2,4-Dinitrotoluene | 2 μg/L | ≤ 1 μg/L |
| 2,6-Dinitrotoluene | 2 μg/L | ≤ 1 μg/L |
| 4,4'-DDE | 0.8 μg/L | ≤ 0.4 μg/L |
| Acetochlor | Reserved[a] | Reserved[a] |
| DCPA mono- and di-acid degradates | 1 μg/L | ≤ 0.5 μg/L |
| EPTC | 1 μg/L | ≤ 0.5 μg/L |
| Molinate | 0.9 μg/L | ≤0.45 μg/L |
| MTBE | 5 μg/L | ≤ 2.5 μg/L |
| Nitrobenzene | 12 μg/L | ≤ 6 μg/L |
| Perchlorate | Reserved[a] | Reserved[a] |
| Terbacil | 2 μg/L | ≤ 1 μg/L |

[a] To be determined.

### 5.4.1 Field Reagent Blank (Shipping or Travel Blank)

EPA Method 524.2 and the approved equivalent methods are the only methods specified in the UCMR that requires the preparation and analysis of a field reagent blank (sometimes referred to as a shipping or travel blank) with each group of samples collected from the same general sample site at approximately the same time. This blank is an aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, storage, preservation, and all analytical procedures. The purpose of this blank is to determine if method contaminants or other interferences are present in the field or shipping environment. If any of the contaminants are detected at concentrations equal to or greater than one half the MRL, consider all data for the problem contaminant(s) for all samples in the shipping batch invalid and flag the monitoring data as not meeting QC criteria. Data not meeting UCMR QC criteria should not be reported to EPA.

## 5.5 Quality Control Sample

Most of the UCMR methods recommend that the laboratory analyze a quality control (QC) sample at least quarterly. A QC sample is a solution of method contaminants of known concentration which is used to spike an aliquot of reagent water or sample matrix. Obtain the QC sample from a source external to the laboratory and different from the source of calibration standards. Use the analysis of the spiked sample it to check laboratory performance.

## 5.6 Sample Matrix Spike and Matrix Spike Duplicate

One technique that is useful in evaluating a laboratory's precision and accuracy for a method is to determine the precision and accuracy of duplicate analyses. To do this, a sample is divided into two or more aliquots in the laboratory, and is processed and analyzed as two separate samples. This technique is only useful when the original sample contains background concentrations of the method contaminants.

To effectively evaluate precision for UCMR contaminants, the EPA is requiring preparation and analysis of a sample matrix spike (MS) and matrix spike duplicate (MSD). A laboratory-spiked MS sample is an aliquot of an environmental sample to which known quantities of the method contaminants are added in the laboratory. A laboratory MSD sample is an additional aliquot of that same environmental sample to which the same known quantities of the method contaminants are added in the laboratory. For the purposes of the UCMR, EPA is not requiring that the standards used to spike the MS/MSD samples be obtained from a second source. Analyze these MS/MSD samples exactly like a typical monitoring sample; the purpose is to determine whether the sample matrix contributes bias to the analytical results. Determine the concentrations of the contaminants in the unspiked sample matrix in a separate aliquot.

Laboratories are required to prepare and analyze MS/MSD samples at the frequencies listed in Table 5.7. Laboratories are required to perform MS/MSD sample analyses on a minimum of 5% of the UCMR samples that are processed together. For methods that involve extractions, divide one sample from each extraction batch into two aliquots (one MS, one MSD), and spike each with a known concentration of the contaminants prior to extraction. Carry the entire set of unspiked sample and MS/MSD samples through the entire extraction and analysis process. For methods that do not involve extractions and for analysis batches of 20 or less, spike and analyze two aliquots of one of

the UCMR samples in the batch. If the analysis batch contains more than 20 UCMR samples, then divide, spike, and analyze two samples.

Note: As described earlier, an extraction batch is defined as all samples prepared/extracted together by the same person(s) during a work day. Therefore, use the same lot of extracting solvent, internal standard spiking solution, and surrogate standard spiking solution for all samples included in a batch. When applicable, derivatize all samples in a batch with the same batch of derivatizing agent. Include a maximum of 20 UCMR samples in an extraction batch. Additionally, an analysis batch is defined as samples analyzed within a 24-hour period with 30 as the maximum number of samples that can be included in one analysis batch.

**Table 5.7 Requirements for Performing Spiked Sample Analyses**

| Method | Method Specifications | UCMR Specifications |
|---|---|---|
| EPA 507<br>D5475-93<br>991.07 | 1 per 20 samples or each sample set whichever is greater | MS/MSD per 20 samples or a batch, whichever is smaller; alternate low-mid-level |
| EPA 508<br>D5812-96<br>990.06 | 1 per 10 samples or each sample set whichever is greater | MS/MSD per 20 samples or a batch, whichever is smaller; alternate low-mid-level |
| EPA 508.1<br>D5812-96<br>992.32 | 1 per sample matrix | MS/MSD per 20 samples or a batch, whichever is smaller; alternate low-mid-level |
| EPA 515.1<br>D5317-93<br>992.32 | 1 per 10 samples or each sample set whichever is greater | MS/MSD per 20 samples or a batch, whichever is smaller; alternate low-mid-level |
| EPA 515.2<br>D5317-93<br>992.32 | 1 per 10 samples or each sample set whichever is greater | MS/MSD per 20 samples or a batch, whichever is smaller; alternate low-mid-level |
| EPA 524.2<br>D5790-95<br>SM6210D<br>SM6200B | Not required unless matrix effects suspected | MS/MSD per 20 samples or a batch, whichever is smaller; alternate low-mid-level |
| EPA 525.2 | 1 per extraction batch 1 per 20 samples | MS/MSD per 20 samples or a batch, whichever is smaller; alternate low-mid-level |

Note: EPA = EPA Methods, D = ASTM Methods, SM = APHA Standard Methods, 900 series = AOAC Methods. See Table 1.5 for the full reference for each analytical method.

The laboratory must choose a spiking concentration from one of the two concentrations listed in Table 5.8. The spiking concentration should be within ± 20% of one of the levels provided in the table. To determine precision data from laboratory MS/MSD samples at the MRL level and at a higher concentration, spike the samples at the concentrations listed in approximately a 50% ratio.

For example, if a set of 40 samples are received, spike two aliquots of a sample from the first 20 samples with the low-level (± 20 % MRL) spike, and spike the MS/MSD for the second set of 20 samples with the mid-level spike.

Laboratories must report all MS/MSD sample recovery data and all data from the batch of samples processed/analyzed with the MS/MSD sample. In addition, laboratories must also report the spiking concentration for all MS/MSD samples. To facilitate this, data element 16, Spiking Concentration, has been included in the data elements required for the UCMR. Values for this data element should only be reported for MS/MSD samples, and the unit of measure for the value reported should match the unit of measure used to report the sample analytical result reported in data element 7, Analytical Result - Value (this unit of measure is reported in data element 8, Analytical Result - Unit of Measure). Data from MS/MSD samples will be used by EPA to evaluate the quality of the monitoring data. Water systems and laboratories may also use these data to determine the appropriateness of the methodology used to analyze the UCMR samples.

EPA plans to use the data from MS/MSD analyses to provide an estimate of the precision and accuracy of measurements made by individual laboratories. Subsets of the UCMR data may be selected for specific modeling or correlational analyses, based on laboratory precision for the contaminants of interest. Laboratories will not be required to meet specific percent recovery or precision requirements for the MS/MSD analyses. Monitoring data will not be rejected based on MS/MSD sample recovery data.

The precision of measurements will be evaluated on the basis of values reported for data element 14, Analytical Precision. For the UCMR, analytical precision is defined as the relative percent difference (RPD) between MS and MSD results. For each analytical result obtained, the laboratories and/or systems must report the RPD for the MS/MSD set analyzed in the same batch of samples as the analytical result being reported. Analytical precision is calculated using the formula:

$$RPD = \frac{|r_1 - r_2|}{\left(\frac{r_1 + r_2}{2}\right)} \times 100$$

RPD = Relative Percent Difference
$r_1$ = matrix spike (MS) analytical result
$r_2$ = matrix spike duplicate (MSD) analytical result

EPA will also be evaluating the analytical accuracy of measurements reported by examining the values reported for data element 15, Analytical Accuracy. Analytical accuracy describes how close a result is to the true value, and is measured through the use of spikes, standards, surrogates or performance evaluation samples. For the purposes of the UCMR, analytical accuracy is defined as the percent recovery of the contaminant in the MS sample analyzed in the same analytical batch as the sample result being reported. To calculate the analytical accuracy, laboratories should use the formula:

$$Percent\ Recovery = \frac{|r_1 - r_3|}{s} \times 100$$

$r_1$ = matrix spike (MS) analytical result
$r_3$ = sample analytical result
s = spiking concentration of matrix spike

**Table 5.8 Concentrations for Spiking MS/MSD Samples**

| Contaminant | Low-Level Spike Concentration | Mid-Level Spike Concentration |
|---|---|---|
| 2,4-Dinitrotoluene | 2 µg/L ± 20 % | ± 20% of mid-level standard |
| 2,6-Dinitrotoluene | 2 µg/L ± 20 % | ± 20% of mid-level standard |
| 4,4'-DDE | 0.8 µg/L ± 20 % | ± 20% of mid-level standard |
| Acetochlor | Reserved [a] | Reserved [a] |
| DCPA mono- and di-acid degradates | 1 µg/L ± 20 % | ± 20% of mid-level standard |
| EPTC | 1 µg/L ± 20 % | ± 20% of mid-level standard |
| Molinate | 0.9 µg/L ± 20 % | ± 20% of mid-level standard |
| MTBE | 5 µg/L ± 20 % | ± 20% of mid-level standard |
| Nitrobenzene | 12 µg/L ± 20 % | ± 20% of mid-level standard |
| Perchlorate | Reserved [a] | Reserved [a] |
| Terbacil | 2 µg/L ± 20 % | ± 20% of mid-level standard |

[a] To be determined.

## 5.7 Internal Standard

Several of the UCMR methods require or recommend the use of an internal standard (IS) for calibration and quantification purposes. An IS is a pure contaminant that is added to a sample or sample extract in a known amount. It is used to measure the relative responses of other method contaminants and surrogates that are components of the same solution. The IS must be a contaminant that is not a sample component. When used, the IS is added to all samples, standards, and QC samples or their extracts.

The methods usually recommend specific compounds and concentrations for use as ISs. When the method provides flexibility in the selection of the IS or IS concentration, EPA allows the same flexibility for analyses of UCMR samples.

The methods vary in their specifications of when the IS is added during the sample processing steps. Some methods require the addition of the IS to the sample prior to any processing, while other methods stipulate the addition to the sample extract immediately prior to instrumental analysis. Laboratories are required to follow the directions in the method when performing analyses for the UCMR.

**Table 5.9 Requirements for Internal Standard Analyses**

| Method | Method Specifications | UCMR Specifications | UCMR Acceptance Criteria |
|---|---|---|---|
| **GC Criteria for Sample Extract IS Response** | | | |
| EPA 507<br>D5475-93<br>991.07 | ≤ 30% deviation from daily calibration check standard's IS response | Same as method | Same as method |
| EPA 508<br>D5812-96<br>990.06 | ≤ 30% deviation from daily calibration check standard's IS response | | |
| EPA 508.1<br>D5812-96<br>992.32 | ± 30% of continuing calibration check standard or ± 50% of initial calibration | | |
| EPA 515.1<br>D5317-93<br>992.32 | ≤ 30% deviation from daily calibration check standard's IS response | | |
| EPA 515.2<br>D5317-93<br>992.32 | ≤ 30% deviation from daily calibration check standard's IS response | | |
| **GC/MS Criteria for IS Response in Continuing Calibration** | | | |
| EPA 524.2<br>D5790-95<br>SM6210D<br>SM6200B | IS response must not have decreased by more than 30% of last continuing calibration or increased by more than 50% of initial calibration | Same as method | Same as method |
| EPA 525.2 | IS response must not have decreased by more than 30% of last continuing calibration or increased by more than 50% of initial calibration | | |

Note: EPA = EPA Methods, D = ASTM Methods, SM = APHA Standard Methods, 900 series = AOAC Methods. See Table 1.5 for the full reference for each analytical method.

The methods also vary in the criteria used to evaluate the IS recovery, when IS techniques are utilized. In general, monitor the detector response to the IS in each sample; it should be relatively constant during the period in which a batch of samples is analyzed. Specific criteria for evaluating

the IS responses are listed in the methods and summarized in Table 5.9. Compare each sample's IS detector response to the average IS detector response obtained for the calibration curve. The acceptance criteria are given as *percentage recovery* which is determined using the following formula:

$$IS\ \%\ Recovery = \frac{Sample\ IS\ Detector\ Response}{Calibration\ Curve\ Average\ IS\ Detector\ Response} \times 100$$

If the IS in a specific sample does not meet the acceptance criteria specified in the method, then consider data from that sample analysis invalid. If possible, re-analyze the sample. If this cannot be done, then the data for that sample are considered invalid for the analysis and should not be reported to EPA.

## 5.8 Surrogate Standard

Several of the UCMR methods require the use of surrogate analytes. A surrogate is a pure analyte which is extremely unlikely to be found in any sample. It is added to a sample aliquot in a known amount before the sample is processed, and is measured with the same procedures used to measure other sample target contaminants. The purpose of a surrogate analyte is to monitor method performance with each sample. When used, the surrogate is added to all samples, standards, and QC samples.

The methods usually recommend specific compounds and concentrations for use as surrogate standards. When the method provides flexibility in the selection of the surrogate standard or its concentration, EPA allows the same flexibility for analyses of UCMR samples.

Table 5.10 lists the UCMR methods that require surrogates as well as percent recovery acceptance criteria where specified by the appropriate methods.

For EPA Methods 524.2 and 525.2, the surrogate criteria are listed in Section 10.2.6.1 of each method.

There are two techniques for monitoring the surrogate standard. If the method specifies that the same concentration of surrogate standard must be added to all samples, standards and QC samples, then compare the surrogate detector response in each analysis to the average surrogate detector response obtained for the calibration curve. The acceptance criteria are given as *percentage recovery* which is determined using the following formula:

$$Surrogate\ \%\ Recovery = \frac{Sample\ Surrogate\ Detector\ Response}{Calibration\ Curve\ Average\ Surrogate\ Detector\ Response} \times 100$$

Some methods recommend preparing a calibration curve for the surrogate standard similar to the preparation of a curve for each of the method contaminants. In those cases, the acceptance criteria are given as *percentage recovery* which is determined using the following formula:

$$\textit{Surrogate \% Recovery} = \frac{\textit{Measured Surrogate Concentration}}{\textit{Expected Surrogate Concentration}} \times 100$$

If the surrogate in a specific sample does not meet the acceptance criteria, re-analyze the sample if possible. If this cannot be done, then the data for that sample are considered suspect for the analysis in question, and should not be reported to EPA.

EPA recognizes that failure to meet the surrogate standard recovery criteria could be the result of matrix interferences in a small number of instances. Even if this is the reason for failure, the data are suspect for all the contaminants in the analysis.

**Table 5.10 Requirements for Surrogate Standard Analyses**

| Method | Method Specified Surrogate Recovery | UCMR Specifications | UCMR Acceptance Criteria |
|---|---|---|---|
| EPA 507<br>D5475-93<br>991.07 | ± 30% | Same as method | Same as method |
| EPA 508<br>D5812-96<br>990.06 | ± 30% | | |
| EPA 508.1<br>D5812-96<br>992.32 | ± 30% | | |
| EPA 515.1<br>D5317-93<br>992.32 | ± 30% | | |
| EPA 515.2<br>D5317-93<br>992.32 | ± 40% | | |
| EPA 524.2<br>D5790-95<br>SM6210D<br>SM6200B | ± 30% | | |
| EPA 525.2 | ± 30% | | |

Note: EPA = EPA Methods, D = ASTM Methods, SM = APHA Standard Methods, 900 series = AOAC Methods. See Table 1.5 for the full reference for each analytical method.

## 5.9 Confirmation

### 5.9.1 Gas Chromatographic Methods

Preliminary identification of contaminant compounds using EPA Methods 507, 508, 508.1, 515.1, and 515.2, as well as in the approved alternative methods (see Table 1.5), is performed by comparison of the target contaminant retention time to the retention time of a standard reference chromatogram. If the retention time of an unknown contaminant corresponds, within standard acceptable limits, to the retention time of a standard reference compound, then identification is presumed positive. The UCMR requires analytical confirmation by gas chromatographic/mass spectrometry (GC/MS) of positive identification, either using results of the primary column alone or with the added secondary column information.

The length of the retention time window used to make identifications should be based on measurements of actual retention time variations of standards over the course of a day. A suggested window size for a particular contaminant can be calculated using three times the standard deviation of a retention time for that particular contaminant. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

Identification requires expert judgement when sample components are not resolved chromatographically. When peaks obviously represent more than one sample contaminant (i.e., a broadened peak with shoulder[s] or a valley between two or more maxima), or any time when doubt exists over the identification of a peak on a chromatogram, use appropriate alternative techniques to help confirm peak identification. Positive identification of contaminants is required for results by GC/MS. False positives can be minimized by the use of a second dissimilar chromatography column. Primary columns and suggested alternative dissimilar confirmation columns are described in each of the methods. GC/MS analysis for confirmation is not necessary if positive results from the primary column are not confirmed by the secondary dissimilar column.

### 5.9.2 Gas Chromatography/Mass Spectrometry Confirmation

The UCMR requires confirmation of any contaminant detected above the MRL by Gas Chromatography/Mass Spectrometry (GC/MS) methods. Laboratories have the option of confirming the presence of an analyte using a second chromatography column prior to submitting the sample for GC/MS analyses, or may go directly from the primary column analyses to GC/MS confirmation. If the contaminant detection is confirmed by the secondary column, then reconfirm the contaminant by GC/MS using three specified ion peaks for contaminant identification. Recommended ion peaks for identification purposes are listed in Table 5.11. The UCMR allows single point calibration of the GC/MS system for confirmation purposes only as long as the calibration standard is at a concentration within ± 50% of the concentration determined by the initial analysis. As an option, laboratories may prefer to perform a three-point calibration with single point daily calibration verification of the GC/MS system regardless of whether that verification standard concentration is within ± 50% of sample response. If GC/MS analysis confirms the initial contaminant detection, report the results determined from the initial analysis.

**Table 5.11 Recommended Confirmation Ions**

| Contaminant | Recommended Confirmation Ions |
|---|---|
| 2,4-dinitrotoluene | 63, 89, 165 |
| 2,6-dinitrotoluene | 63, 89, 165 |
| 4,4'-DDE | 246, 316, 318 |
| Acetochlor | Reserved[a] |
| DCPA dimethyl ester | 299, 300, 302 |
| EPTC | 86, 128, 189 |
| Molinate | 83, 126, 187 |
| MTBE | 41, 57, 73 |
| Nitrobenzene | 51, 77, 123 |
| Perchlorate | Reserved[a] |
| Terbacil | 116, 160, 161 |

Note: These ions are recommended for use in confirming all positive results. However, since mass spectrometers using different mass selection techniques may display spectra with different mass intensities, the analyst may to choose alternate ions that better characterize the spectra displayed by their mass spectrometer.

[a] To be determined.

### 5.9.3 Mass Spectrometry Methods

Perform identification and confirmation of a contaminant using EPA Methods 524.2 and 525.2 by comparison of the contaminant's mass spectrum (after background subtraction) to a reference spectrum in the user-created database. For the DCPA degradates, confirm the identification by injecting the extract obtained during the primary analyses into a mass spectrometer. The GC retention time of the contaminant should be within three standard deviations of the mean retention time of the reference contaminant in the calibration mixture.

In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample and should agree within ±20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample (contaminant) spectrum should be in the range of 10-50%. Some ions, particularly the molecular ions, are of special importance and should be evaluated even if they are below 10% relative abundance.

Identification requires expert judgment when sample contaminants are not resolved chromatographically and produce mass spectra containing ions that are contributed by more than one contaminant. When GC peaks obviously represent more than one sample contaminant (i.e., a broadened peak with shoulder[s] or a valley between two or more maxima), select appropriate contaminant spectra and background spectra by examining plots of characteristic ions for tentatively identified contaminants. When target contaminants co-elute (i.e., when only one GC peak is

apparent for two or more contaminants), the identification criteria can be met, but each contaminant spectrum will contain extraneous ions contributed by the co-eluting contaminants. Because purgeable organic compounds (such as those for some UCMR contaminants) are relatively small molecules and produce comparatively simple mass spectra, this is not a significant problem for most contaminants determined according to EPA Method 524.2.

Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC or retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs.

## 5.10 Additional Quality Controls

The laboratory must examine the samples when they arrive in the laboratory to determine if the proper shipping procedures were used and the required shipping conditions were maintained. Samples requiring storage at 4°C (± 2°) should arrive at the laboratory packed in ice or frozen cold packs. If there is no visible ice or the cold packs are completely thawed, the laboratory should report the conditions to the water system. Samples should not be analyzed if they were not shipped properly and/or if they did not arrive in the required condition. As the UCMR specifies that resampling is required within 14 days of the observance of a sampling error, the laboratory should immediately contact the water system and arrange for resampling. If resampling cannot be performed within this time period, then the water system should indicate in the report to EPA that the samples were invalidated because of a shipment problem and no data should be reported.

The laboratory also must invalidate samples that were collected in improper sampling containers (e.g., plastic bottles instead of glass) or that were improperly filled (e.g., half-filled bottles for samples that are required to be completely full). As above, the laboratory should immediately contact the water system and arrange for resampling within the required 14 days. If resampling cannot be performed within this time period, then the water system should indicate in the report to EPA that the samples were invalidated because of a sampling error and no data should be reported.

Finally, the laboratory must ensure each sample is analyzed within the required holding time. A list of applicable holding times is presented in Table 5.12. When appropriate, EPA standardized the holding times across analytical methods for the same contaminant group.

**Table 5.12 Maximum Holding Times for Samples and Extracts**

| Approved Analytical Methods | Sample | Extract |
|---|---|---|
| EPA 507<br>D5475-93<br>991.07 | 14 days | 14 days |
| EPA 508<br>D5812-96<br>990.06 | 7 days | 14 days |

| Approved Analytical Methods | Sample | Extract |
|---|---|---|
| EPA 508.1<br>D5812-96<br>992.32 | 14 days | 30 days |
| EPA 515.1<br>D5317-93<br>992.32 | 14 days | 28 days |
| EPA 515.2<br>D5317-93<br>992.32 | 14 days | 14 days |
| EPA 524.2<br>D5790-95<br>SM6210D<br>SM6200B | 14 days | Not Applicable |
| EPA 525.2 | 14 days | 30 days from collection |

Note: EPA = EPA Methods, D = ASTM Methods, SM = APHA Standard Methods, 900 series = AOAC Methods. See Table 1.5 for the full reference for each analytical method.

If a UCMR sample is not extracted or analyzed within the times specified in Table 5.12, then the data for the sample should not be reported. The laboratory should indicate to the water system that the sample was invalidated because of a holding time problem. This information would then be reported to EPA when the system submits its report for that sampling period.

# Section 6. Additional Analytical Method Specifications

## 6.1 Clarifications Concerning EPA Methods 515.1 and 515.2 and the Approved Equivalent Methods

EPA Methods 515.1 and 515.2, as well as their equivalent voluntary consensus standards (D5317-93 and 992.32), have been approved for use in measuring the DCPA mono- and di-acid degradates under the UCMR (see Table 1.5). However, EPA is specifically requiring that the methylene chloride wash listed in Sections 11.1.4 and 11.1.5 of the EPA Methods (Sections 12.1.4 and 12.1.5 of D5317-93 and Section F(a) of 992.32) be performed. The use of this wash is being emphasized in the QC requirements because it washes away the parent compound, DCPA.

If this wash is not performed, the data generated will reflect not just the total of the mono- and di-acid degradates of DCPA, but will include the concentration of the parent compound in addition to the concentration of the two degradates. As noted previously, because the approved methods do not allow for the identification and quantification of the individual acids, the single analytical result obtained from these methods should be reported as total DCPA mono- and di-acid degradates.

## 6.2 Recommendations for EPA Method 524.2 and the Approved Equivalent Methods

Although EPA is not altering the method specifications for EPA Method 524.2 for use with the UCMR, EPA emphasizes that laboratories should use the three stage trap listed in Section 6.2.2 of the Method [Section 7.2.2.1 of D5790.95, Section 3 of SM6210D, and Section 2(a)(2) of SM6200B]. Alternate traps may not be capable of retaining adequate concentrations of nitrobenzene, therefore, nitrobenzene can not be detected at reasonable concentrations in either standards or samples. Thus, the data generated for nitrobenzene with this method will not be capable of meeting the strict quality control requirements specified in the UCMR and in this Manual.

# Section 7. Reporting

## 7.1 Public Water Systems Reporting to EPA

The appropriate and consistent reporting of UCMR monitoring data from the participating Public Water Systems (PWSs) is critical to EPA's efforts to evaluate the data for future regulatory development. The UCMR monitoring data are reported according to specific "data elements" through the Safe Drinking Water Information System/Federal Information System (SDWIS/FED) for inclusion in the NCOD.

The PWSs are required to report the UCMR monitoring data to EPA for evaluation. The UCMR contaminant occurrence data will be included in the NCOD and will be made available to the public. For a detailed description of reporting responsibilities and requirements, refer to the *Unregulated Contaminant Monitoring Regulation Reporting Guidance*, the *Unregulated Contaminant Monitoring Regulation Guidance for Operators of Public Water Systems Serving 10,000 or Fewer People*, and the *Unregulated Contaminant Monitoring Regulation Integrated Guidance Document*, all available from the EPA Water Docket, telephone (202) 260-3027, Docket Number W-98-02.

Monitoring data for all contaminants must be reported according to contaminant type and must include 17 specific data elements for each contaminant. The required data elements are listed in Table 7.1. Many of the data elements will be furnished by the laboratory to the PWS and the PWS will provide the remainder of the data elements. A brief definition of each data element is also included. PWSs can arrange to have laboratories report analytical data directly to EPA. However, the PWSs retain final responsibility to ensure that all monitoring data is reported. In this regard, the final reporting responsibility of the PWS is the same as for SDWA compliance monitoring.

The required data elements will help to optimize the utility and quality of UCMR analytical data. The reporting of the data elements listed in Table 7.1 is important to provide details needed to evaluate possible regulatory development related to UCMR contaminants and methods.

### 7.1.1 Reporting of Results Obtained for the DCPA Mono- and Di-Acid Degradates

The analytical methods approved under the UCMR for measuring the DCPA mono- and di-acid degradates do not, as approved, allow for the identification and quantification of the individual acids. To provide for the consistent reporting of results to the NCOD and to avoid confusion, EPA is specifying that the single analytical result obtained from these methods should be reported as total DCPA mono- and di-acid degradates. As a result, data element 5, Contaminant/Parameter, will not have as acceptable values "DCPA mono-acid degradate" or "DCPA di-acid degradate." Instead, the appropriate acceptable value for this data element will be "Total DCPA mono- and di-acid degradates."

### 7.1.2 Reporting of Data Below the Specified Minimum Reporting Level

As previously mentioned in Section 5.1 of this Manual, EPA recognizes that some laboratories are able to provide reliable data at concentrations lower than the MRLs specified in the UCMR. To achieve consistency in the NCOD, laboratories are only required to report quantitative results for concentrations equal to or greater than the MRLs. However, EPA also recognizes the usefulness of

receiving more complete results to allow evaluation of the analytical method implementation. Systems and laboratory that are able to reliably report results below the MRL are encouraged to do so. To report reliable results obtained below the MRL, laboratories and/or water systems should do three things:

1) For data element 6, Analytical Results - Sign, report a "<," indicating that the result obtained is less than the MRL listed in Table 5.1.

2) For data element 7, Analytical Result - Value, report the actual concentration value obtained for the contaminant.

3) For data element 17, Presence/Absence, report the contaminant as "Present."

The combination of these three steps will allow for the reporting of data below the MRL, and will enable EPA to more fully evaluate the MRL for the respective contaminant and assist in determining what the final MRL might be if EPA requires future monitoring of the contaminant.

### 7.1.3 Reporting of Water Quality Parameter Data

As mentioned in Section 3.2 of this Manual, the revised UCMR specifies that certain chemical and physical parameters must be measured in the field at each sampling point from which UCMR samples are collected. These parameters are being required because they are important indicators of water quality and may contribute to the likelihood of the contaminants being found in drinking water. EPA believes that these parameters will allow for a more thorough scientific understanding of the occurrence of unregulated contaminants. As all UCMR (1999) List 1 contaminants are chemicals, EPA is only requiring that the pH of the water being sampled is measured and reported. The pH of the water being sampled must be reported along with other UCMR (1999) List 1 data. To facilitate this reporting, data element 5, Contaminant/Parameter, will have "pH" as an acceptable value.

## 7.2 Public Notification of Results (Report of PWS to Consumers)

The results of UCMR monitoring will be reportable through the Consumer Confidence Reports (CCR), as required by SDWA §1441(c)(4)(B) and the Consumer Confidence Reports (CCR) regulation (63 FR 44512), as well as through the revised Public Notification Rule (PNR) proposed on May 13,1999 (64 FR 25964) and expected to be finalized by late 1999. It is anticipated that reporting through the PNR and CCR rules would satisfy the notification provision for unregulated contaminants. Failure to monitor for unregulated contaminants required through the UCMR would be reportable under the PNR.

The results reported through the PNR and CCR rules should be based on the same monitoring data EPA and the States will receive. UCMR data will be submitted to SDWIS/FED for inclusion in the NCOD. Information in the NCOD will be available to the public.

Reporting of unregulated contaminants not on the UCMR (1999) List is not required by EPA under the CCR or PNR, except as directed by the State. Therefore, any "emerging" contaminants of local or State concern alternatively could be reported voluntarily to the NCOD. This reporting would assist in the determination of whether an emerging contaminant is a problem of national extent and should be considered for health-based standards or advisories. EPA will issue guidance explaining

how data on the occurrence of contaminants not on the UCMR (1999) List may be voluntarily reported to the NCOD.

Large PWSs may also wish to report previously collected data on the occurrence of UCMR (1999) List 1 contaminants in lieu of participating in Assessment Monitoring. To ensure the quality of data included in the NCOD, EPA is requiring that any data previously collected and submitted in lieu of UCMR monitoring must meet *all* analytical method and quality control requirements specified in the UCMR and in this Manual.

**Table 7.1 UCMR Reporting Requirements Sample Data Elements**

| Data Element | Definition |
|---|---|
| 1. Public Water System (PWS) Identification Number | The code used to identify each PWS. The code begins with the standard two-character postal State abbreviation; the remaining seven characters are unique to each PWS. |
| 2. Public Water System Facility Identification Number - Source, Treatment Plant, and Sampling Point | An identification number established by the State, or, at the State's discretion, the PWS, that is unique to the system for an intake for each source of water, a treatment plant, and a sampling point. Within each PWS, each intake, treatment plant, and sampling point must receive a unique identification number, including, for intake; surface water intake, ground water well, or wellfield centroid; and including, for sampling point; entry points to the distribution system, wellhead, intake, locations within the distribution system, or other representative sampling point specified by the State. The same identification number must be used consistently through the history of unregulated contaminant monitoring to represent the facility. |
| 3. Sample Collection Date | The date the sample is collected reported as 4-digit year, 2-digit month, and 2-digit day. |
| 4. Sample Identification Number | A unique identifier assigned by the PWS for each sample. |
| 5. Contaminant/Parameter | The unregulated contaminant or water quality parameter for which the sample is being analyzed. |
| 6. Analytical Results - Sign | An alphanumeric value indicating whether the sample analysis result was:<br>(a) (<) "less than" means the contaminant was not detected or was detected at a level "less than" the MRL.<br>(b) (=) "equal to" means the contaminant was detected at a level "equal to" the value reported in "Analytical Result - Value." |
| 7. Analytical Result - Value | The actual numeric value of the analysis for chemical and microbiological results, or the Minimum Reporting Level (MRL) if the analytical result is less than the specified contaminant's MRL. |
| 8. Analytical Result - Unit of Measure | The unit of measurement for the analytical results reported. [e.g., micrograms per liter, ($\mu$g/L); colony-forming units per milliliter, (CFU/mL), etc.] |
| 9. Analytical Method Number | The identification number of the analytical method used. |

| Data Element | Definition |
|---|---|
| 10. Sample Analysis Type | The type of sample collected. Permitted values include:<br>(a) Field Sample - sample collected and submitted for analysis under this Rule.<br>(b) Batch Spike/Spike Duplicate - Samples associated with a batch used for calculating analytical precision and accuracy. A batch is defined as the set of field samples plus one spiked sample and one spiked duplicate sample to analyzed for contaminant concentrations. |
| 11. Sample Batch Identification Number | A number assigned by the laboratory to the batch of samples analyzed with the spiked sample (at the spiking concentration reported), to be reported as 9-digit laboratory number (assigned by the State or EPA), 4-digit year, 2-digit month, 2-digit day, and 2-digit batch number. |
| 12. Detection Level | "Detection level" is referring to the detection limit applied to both the method and equipment. Detection limits are the lowest concentration of a target contaminant that a given method or piece of equipment can reliably ascertain and report as greater than zero ( e.g., Instrument Detection Limit, Method Detection Limit, or Estimated Detection Limit). |
| 13. Detection Level Unit of Measure | The unit of measure to express the concentration, count, or other value of a contaminant level for the detection level reported. [e.g., micrograms per liter, ($\mu$g/L); colony-forming units per milliliter, (CFU/mL), etc.] |
| 14. Analytical Precision | Precision is the degree of agreement among a set of repeated measurements and is monitored through the use of replicate samples or measurements. For the purposes of the UCMR, Analytical Precision is defined as the relative percent difference (RPD) between spiked matrix duplicates. The RPD for the spiked matrix duplicates analyzed in the same batch of samples as the analytical result being reported is to be entered in this field. Precision is calculated as the RPD between spiked matrix duplicates using;<br>$RPD = [(X_1 - X_2) / \{(X_1 + X_2)/2\}] \times 100$ |
| 15. Analytical Accuracy | Accuracy describes how close a result is to the true value measured through the use of spikes, standards, surrogates or performance evaluation samples. For the purposes of the UCMR, Analytical Accuracy is defined as the percent recovery of the contaminant in the spiked matrix sample analyzed in the same analytical batch as the sample result being reported and calculated using;<br>% recovery = [(amount found in Spiked sample - amount found in sample) / amount spiked] x 100 |
| 16. Spiking Concentration | The concentration of method analytes added to a sample to be analyzed for calculating analytical precision and accuracy where the value reported uses the same unit of measure reported for Analytical Results. |
| 17. Presence/Absence | Chemicals: Presence- a response was produced by the analysis (i.e., greater than or equal to the MDL but less than the MRL)/Absence- no response was produced by the analysis (i.e., less than the MDL).<br>Microbiologicals: Presence- indicates a response was produced by the analysis /Absence- indicates no response was produced by the analysis. |

# Appendix A

## Abbreviations and Acronyms

| | |
|---|---|
| 2,4-DNT | - 2,4-dinitrotoluene |
| 2,6-DNT | - 2,6-dinitrotoluene. |
| 4,4'-DDE | - 4,4'-dichloro dichlorophenyl ethylene, a degradation product of DDT |
| Alachlor ESA | - alachlor ethanesulfonic acid, a degradation product of alachlor |
| AOAC | - Association of Official Analytical Chemists |
| APHA | - American Public Health Association |
| ASDWA | - Association of State Drinking Water Administrators |
| ASTM | - American Society for Testing and Materials |
| BGM | - Buffalo Green Monkey cells, a specific cell line used to grow viruses |
| CAS | - Chemical Abstract Service |
| CASRN | - Chemical Abstract Service Registry Number |
| CCL | - Contaminant Candidate List |
| CCR | - Consumer Confidence Reports |
| CERCLA | - Comprehensive Environmental Response, Compensation & Liability Act |
| CFR | - Code of Federal Regulations |
| CFU | - colony forming unit |
| CFU/mL | - colony forming units per milliliter |
| CWS | - community water system |
| DCPA | - dimethyl tetrachloroterephthalate, chemical name of the herbicide dacthal |
| DCPA mono- and di-acid degradates | - degradation products of DCPA |
| DDE | - dichloro dichlorophenyl ethylene, a degradation product of DDT |
| DDT | - dichloro diphenyl trichloroethane, a general insecticide |
| DNA | - deoxyribonucleic acid |
| EDL | - estimated detection limit |
| EPA | - Environmental Protection Agency |
| EPTC | - s-ethyl-dipropylthiocarbamate, an herbicide |
| EPTDS | - Entry Point to the Distribution System |
| ESA | - ethanesulfonic acid, a degradation product of alachlor |
| FACA | - Federal Advisory Committee Act |
| FTE | - full-time equivalent |
| GC | - gas chromatography, a laboratory method |
| GLI method | - Great Lakes Instruments method |
| GW | - ground water |
| GUDI | - ground water under the direct influence (of surface water) |
| HPLC | - high performance liquid chromatography, a laboratory method |

| | |
|---|---|
| ICR | - Information Collection Request / Rule |
| IRFA | - initial regulatory flexibility analysis |
| IMS | - immunomagnetic separation |
| IRIS | - Integrated Risk Information System |
| IS | - internal standard |
| LLE | - liquid/liquid extraction, a laboratory method |
| MAC | - *Mycobacterium avium* complex |
| MOA | - Memorandum of Agreement |
| MCL | - maximum contaminant level |
| MDL | - method detection limit |
| MRL | - minimum reporting level |
| MS | - mass spectrometry, a laboratory method |
| MS | - sample matrix spike |
| MSD | - sample matrix spike duplicate |
| MTBE | - methyl tertiary-butyl ether, a gasoline additive |
| NAWQA | - National Water Quality Assessment Program |
| NCOD | - National Drinking Water Contaminant Occurrence Database |
| NDWAC | - National Drinking Water Advisory Council |
| NERL | - National Environmental Research Laboratory |
| NPS | - National Pesticide Survey |
| NTIS | - National Technical Information Service |
| NTNCWS | - non-transient non-community water system |
| NTTAA | - National Technology Transfer and Advancement Act |
| OGWDW | - Office of Ground Water and Drinking Water |
| OMB | - Office of Management and Budget |
| PAH | - Poly-aromatic hydrocarbon |
| PB | - particle beam |
| PBMS | - Performance-Based Measurement System |
| pCi/L | - picocuries per liter |
| PCR | - polymerase chain reaction |
| $^{210}$Pb | - Lead-210 (also Pb-210), a lead isotope and radionuclide; part of the uranium decay series |
| $^{210}$Po | - Polonium-210 (also Po-210), a polonium isotope and radionuclide; part of the uranium decay series |
| PWS | - Public Water System |
| PWSF | - Public Water System Facility |
| QA | - quality assurance |
| QC | - quality control |
| RDX | - royal demolition explosive, hexahydro-1,3,5-trinitro-1,3,5-triazine |
| RFA | - Regulatory Flexibility Act |
| RPD | - relative percent difference |
| RSD | - relative standard deviation |

| | |
|---|---|
| SBREFA | - Small Business Regulatory Enforcement Fairness Act |
| SD | - standard deviation |
| SDWA | - Safe Drinking Water Act |
| SDWIS | - Safe Drinking Water Information System |
| SDWIS FED | - the Federal Safe Drinking Water Information System |
| SM | - Standard Methods |
| SMF | - Standard Compliance Monitoring Framework |
| SOC | - synthetic organic compound |
| SPE | - solid phase extraction, a laboratory method |
| SRF | - State Revolving Fund |
| STORET | - Storage and Retrieval System |
| SW | - surface water |
| TBD | - to be determined |
| TNCWS | - transient non-community water system |
| UCMR | - Unregulated Contaminant Monitoring Regulation/Rule |
| UCM | - Unregulated Contaminant Monitoring |
| UMRA | - Unfunded Mandates Reform Act of 1995 |
| USEPA | - United States Environmental Protection Agency |
| UV | - ultraviolet |
| VOC | - volatile organic compound |
| µg/L | - micrograms per liter |

# Appendix B

## Definitions

*All monitored systems* means all community water systems serving more than 10,000 people, and the national representative sample of community and non-transient non-community water systems serving 10,000 or fewer people that are selected to be part of a State Plan for the UCMR.

*Assessment Monitoring* means sampling, testing, and reporting of listed contaminants that have available analytical methods and for which preliminary data indicate their possible occurrence in drinking water. All monitored systems must conduct Assessment Monitoring. Assessment Monitoring will be conducted for the UCMR (1999) List 1 contaminants.

*Index systems* means a limited number of small CWSs and NTNCWSs, randomly selected from the systems in State Plans, that must monitor for UCMR contaminants and also additionally must report information on system operating conditions (such as water source, pumping rates, and environmental setting). These systems must monitor and report quarterly each year of the 5-year UCMR cycle with EPA paying for all reasonable monitoring costs. This more detailed and regular monitoring of contaminants and operating conditions will provide important information with which EPA can more fully evaluate conditions under which systems operate and will enable comparisons between system operations of similar size and characteristics.

*Listed contaminant* means a contaminant identified as an analyte in Table 1, 141.40(a)(3) of the Unregulated Contaminant Monitoring Regulation (UCMR). To distinguish the current 1999 UCMR listed contaminants from potential future UCMR listed contaminants, all references to UCMR contaminant lists will identify the appropriate year in parenthesis immediately following the acronym UCMR and before the referenced list. For example, the contaminants included in the UCMR (1999) List include the component lists identified as UCMR (1999) List 1, UCMR (1999) List 2 and UCMR (1999) List 3 contaminants.

*Listing cycle* means the 5-year period for which each revised UCMR list is effective and during which no more than 30 unregulated contaminants from the list may be required to be monitored. EPA is mandated to develop and promulgate a new UCMR List every 5 years.

*Monitoring* means (as distinct from Assessment Monitoring), all aspects of determining the quality of drinking water relative to the listed contaminants. These aspects include drinking water sampling and testing, and the reviewing, reporting, and submission to EPA of analytical results.

*Most vulnerable systems (*or *Systems most vulnerable)* means a subset of 5 to not more than 25 systems of all monitored systems in a State that are determined by that State in consultation with the EPA Regional Office to be most likely to have the listed contaminants occur in their drinking waters, considering the characteristics of the listed contaminants, precipitation, system operation, and environmental conditions (soils, geology and land use).

*Pre-Screen Testing* means sampling, testing, and reporting of the listed contaminants that may have newly emerged as drinking water concerns and, in most cases, for which methods are in an early stage of development. Pre-Screen Testing must be conducted by a limited number of systems (up to 200). The Pre-Screen Testing systems will be selected through the use of a random number generator, and from a list comprised of the States' nominations of up to 25 of the most vulnerable

systems per State. Pre-Screen Testing will be performed to determine whether a listed contaminant occurs in sufficient frequency in the most vulnerable systems or sampling locations to warrant its being included in future Assessment Monitoring or Screening Surveys. Pre-Screen Testing will be conducted for the UCMR (1999) List 3 contaminants.

*Random Sampling* is a statistical sampling method by which each member of the population has an equal probability (an equal random chance) of being selected as part of a sample (the sample being a small subset of the population which represents the population as a whole).

*Representative Sample* means a subset of community and non-transient non-community water systems serving 10,000 or fewer people which EPA selects using a random number generator to obtain public water system identification numbers to place them on the first representative sample list. The selection is weighted by population served within a State, water source and then by size categories of 10,000 to 3,301 people, 3,300 to 501 people, and 500 or fewer people; a State may substitute systems from a replacement list of such systems derived through the same method for systems in the first list because a system on the first list is closed, merged or purchases water from another system.

*Sampling* means the act of collecting water from the appropriate location in a public water system (from the applicable point from an intake or well to the end of a distribution line, or in some limited cases, a residential tap) following proper methods for the particular contaminant or group of contaminants.

*Sampling Point* means a unique location where UCMR samples are to be collected.

*Screening Survey* means sampling, testing, and reporting of the listed contaminants for which analytical methods are recently developed and have uncertain potential for occurrence in drinking water by a subset of approximately 300 systems from all monitored systems selected through use of a random number generator for public water system identification numbers. These systems must conduct the Screening Survey for the listed contaminants after public notice and comment to determine whether a listed contaminant occurs at a sufficient frequency and concentration (or density) to warrant being included in future Assessment Monitoring. Two Screening Surveys will be conducted for the UCMR (1999) List 2 contaminants.

*State* means, for the purposes of this section, each of the fifty States, the District of Columbia, U.S. Territories, and Tribal lands. For the national representative sample, Guam, the Commonwealth of Puerto Rico, the Northern Mariana Islands, the Virgin Islands, American Samoa, and the Trust Territories of the Pacific Islands are treated as a State. Any Indian Tribe which has status as a State under Section 1451 of the Safe Drinking Water Act for this program will be considered as a State.

*State Monitoring Plan (*or *State Plan)* means a State's portion of the national representative sample of CWSs and NTNCWSs serving 10,000 or fewer people which must monitor for unregulated contaminants. A State Plan may be developed by a State's acceptance of EPA's representative sample for that State, or by a State's selection of systems from a replacement list (provided by EPA) to replace original systems listed that are determined to be closed or merged, or that purchase water from another system. The State Plan may be part of the State-EPA Memorandum of Agreement that will also include a process by which the State will inform each public water system of its selection for the plan and of its responsibilities to monitor. A State Plan will also include the systems required to conduct Pre-Screen Testing, selected from the State's designation of vulnerable systems.

*Stratified Random Sampling* is a procedure to draw a random sample from a population that has been divided into subpopulations or strata, with each stratum comprised of a population subset sharing common characteristics. Random samples are selected from each stratum proportional to that stratum's proportion of the entire population. The aggregate random sample (compiled from all the strata samples) provides a random sample of the entire population that reflects the proportional distribution of characteristics of the population. In the context of the UCMR, the population of public water systems was stratified by size category (based on population served by the water system) and by the system's water source type (ground water or surface water). This stratification was done to ensure that systems randomly selected as nationally representative sample systems would proportionally reflect the actual number of size and water type categories nationally.

*Testing* means, for the UCMR and distinct from *Pre-Screen Testing*, the submission and/or shipment of samples following appropriate preservation practices to protect the integrity of the sample; the chemical, radiological, physical and/or microbiological analysis of samples; and the reporting of the sample's analytical results for evaluation. Testing is a subset of activities defined as *monitoring*.

*Unregulated contaminants* means chemical, microbiological, radiological and other substances that occur in drinking water or sources of drinking water that are not currently regulated under the federal drinking water program. EPA has not issued standards for these substances in drinking water (i.e., maximum contaminant levels or treatment technology requirements). EPA is required by Congress to establish a program to monitor for selected unregulated contaminants in public water systems to determine whether they should be considered for future regulation to protect public health. The selected contaminants are listed in 141.40(a)(3), Table 1, the UCMR List.

*Vulnerable time* (or *vulnerable period*) means the time (or, in some cases, the 3-month quarter) of the year determined as the most likely to have the listed group of contaminants present at their highest concentrations or densities in drinking water. The vulnerable determination, in the case of the UCMR, is made by the EPA or by the State (under arrangement with the EPA) for a system, subset of systems, or all systems in a State. The vulnerable determination is based on characteristics of the contaminants, precipitation, system operations, and environmental conditions such as soil types, geology, and land use. This determination does not indicate or imply that the listed contaminants will be identified in the drinking water with certainty, but only that sampling conducted during the vulnerable period presumably has the highest likelihood of identifying those contaminants in higher concentrations relative to other sampling times of the year, if and when the contaminants occur.

# Appendix C

## Procedure for Determination of Method Detection Limits

### Definition

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

### Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample. The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

### Procedure

1. Make an estimate of the detection limit using one of the following:

    1. The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

    2. The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

    3. That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

    4. Instrumental limitations. It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interfering concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interfering). The interfering concentration is presupposed to be normally distributed in representative samples of a given matrix.

3.

(a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4. If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit. If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample with a lower level of analyte in the same matrix if possible.

(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4.

(a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will:

(1) prevent repeating this entire procedure when the costs of analyses are high, and

(2) ensure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S<SUP>2</SUP>) and standard deviation (S) of the replicate measurements, as follows:

$$S^2=\frac{1}{n-1}[\sum_{i=1s}^{n} x_i^2-\frac{(\sum_{i=1s}^{n} X_i)^2}{n}]S=(S^2)^{1/2}$$

where:

$X_i$; i = 1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots and $\sum$ refers to the sum of the X values from i=1 to n.

6.

(a) Compute the MDL as follows:

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

where:

MDL = the method detection limit $t_{(n-1,\ 1-\alpha=0.99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. (See Table.)
S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution ($x^2$/df).

LCL = 0.64 MDL
UCL = 2.20 MDL

where:

LCL and UCL are the lower and upper 95% confidence limits, respectively, based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use $S^2$ from the current MDL calculation and $S^2$ from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger $S^2$ into the numerator $S^2_A$ and the other into the denominator $S^2_B$. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows:

if $S^2_A/S^2_B<3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled}=[\frac{6S_A^2+6S_B^2}{12}]^{1/2}$$

if $S^2_A/S^2_B<3.05$, re-spike at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the $S_{pooled}$ as calculated in 7b to compute The final MDL according to the following equation:

MDL=2.681 ($S_{pooled}$)

where 2.681 is equal to $t_{(12,\ 1-\alpha=0.99)}$.

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from percentiles of the chi squared over degrees of freedom distribution.

LCL=0.72 MDL
UCL=1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits, respectively, based on 14 aliquots.

**Table of Students' t Values at the 99 Percent Confidence Level**

| Number of replicates | Degrees of Freedom (n-1) | $t_{(cn-1,.99)}$ |
|---|---|---|
| 7 | 6 | 3.143 |
| 8 | 7 | 2.998 |
| 9 | 8 | 2.896 |
| 10 | 9 | 2.821 |
| 11 | 10 | 2.764 |
| 16 | 15 | 2.602 |
| 21 | 20 | 2.528 |
| 26 | 25 | 2.485 |
| 31 | 30 | 2.457 |
| 61 | 60 | 2.390 |
| 00 | 00 | 2.326 |

**Reporting**

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

(This procedure is from *Title 40–Protection of Environment, Chapter I–Environmental Protection Agency, Part 136–Guidelines Establishing Test Procedures for the Analysis of Pollutants. Appendix B to Part 136--Definition and Procedure for the Determination of the Method Detection Limit--Revision 1.11.) [49 FR 43430, Oct. 26, 1984; 50 FR 694, 696, Jan. 4, 1985, as amended at 51 FR 23703, June 30, 1986]*