Disinfectants and Disinfection Byproducts Rule (DBPR)

Sample Collection and Preservation Procedures

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EPA Approved Analytical Methods

Analyte	Method			Laboratory Certification and Approval*
	EPA	Standard Method	Other	
Chlorine (free, combined, and total)		4500-Cl D 4500-Cl F 4500-Cl G	ASTM D1253-86	Approved Party
Chlorine (total)		4500-Cl E 4500-Cl I		Approved Party
Chlorine (free)		4500-Cl H		Approved Party
Chlorine Dioxide		4500-ClO_2 D 4500-ClO_2 E		Approved Party
TTHM Chloroform Bromoform Bromodichloromethane Dibromochloromethane	502.2 524.2 551.1			Certified Laboratory
HAA5 Monochloroacetic Acid Dichloroacetic Acid Trichloroacetic Acid Monobromoacetic Acid Dibromoacetic Acid	552.1 552.2	6251 B		Certified Laboratory
Bromate	300.1			Certified Laboratory
Bromide	300.0 300.1			Certified Laboratory
Chlorite (monthly)	300.0 300.1			Certified Laboratory
Chlorite (daily)		4500-ClO_2 E		Approved Party
TOC/DOC		5310 B 5310 C 5310 D		Certified Laboratory
UV_{254}		5910 B		Certified Laboratory
Alkalinity		2320 B	ASTM D1067-92B USGS I-1030-85	Approved Party
pH	150.1 150.2	4500-H^+B	ASTM D1293-95	Approved Party
Magnesium hardness	200.7	3111 B 3120 B 3500-Mg E	ASTM 511-93 A 511-93 B	Approved Party

***Note:** According to the National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts; Final Rule, 40 CFR 141.131, systems must use only the analytical methods specified in this table, or otherwise approved by EPA to demonstrate compliance with the DBPR. Analysis for TTHM, HAA5, bromate, bromide, chlorite (monthly), TOC/DOC and UV_{254} must be conducted by a laboratory that has received certification by the Department. Measurements for residual disinfectant concentrations,

chlorite (daily), alkalinity, pH and magnesium hardness may be performed by a party approved by the Department.

General Sample Collection Procedures

We are providing the following information to help you collect drinking water samples for compliance with the DBPR. As each laboratory may use any of the methods in this manual, please confirm with your laboratory the exact procedure you must use to collect and preserve your samples.

General Procedures:

Sample containers and preservatives may be specific to each analytical method. Pay special attention to the sampling equipment indicated for each method.

Quality Assurance/Quality Control (QA/QC):

Your laboratory may ask you to collect duplicate or field/trip blank samples as part of their quality assurance/quality control program. These QA/QC samples are analyzed at no cost to you.

Field duplicates are two separate samples collected at the same time and place, under identical circumstances, and treated exactly the same throughout field and laboratory procedures. Analysis of duplicate samples gives a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

Field blanks are prepared in the field using laboratory-supplied reagent water. Reagent water is placed in a sample container and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. Trip blanks are prepared in the laboratory using reagent water. Trip blanks are carried to the sampling site and are retuned to the laboratory, un-opened. The purpose of the field or trip blank is to determine if method analytes or other interferences are present in the field environment.

Record Keeping:

Fill out labels provided by your laboratory using waterproof ink. At a minimum, include the date, time, sample location and collector name. Make a record of the sampling event for your files. Fill out sample submission forms, as required.

Shipping/Handling:

Maintain a record of chain-of-custody. If you are not personally hand-delivering the samples to the laboratory, consider affixing a tamper-evident seal to each bottle.

To guarantee that holding times for the analytical parameters are not exceeded, ship or deliver samples to the laboratory on the day they are collected. Ice or refrigerate all samples at 4°C from the time of collection to analysis.

Chlorine Residual (free, combined, and total)

Maximum holding time: Analyze immediately

Chlorine is the most commonly used disinfectant in the drinking water treatment industry.

Chlorine applied to water in its molecular or hypochlorite form undergoes hydrolysis to form free chlorine consisting of aqueous molecular chlorine, hypochlorous acid, and hypochlorite ion.

Free chlorine reacts readily with ammonia and certain nitrogenous compounds to form combined chlorine (chloramines).

Total chlorine measurement includes both free and combined chlorine forms.

Sampling Equipment:

Container: 250 mL plastic bottle.
Preservative: None. Analyze sample immediately.
Other:

- Field log book
- Labels/marker
- Gloves and goggles

Sample Collection Procedure:

1. Remove aerator and screen.
2. Turn on cold water tap and allow system to flush until water temperature has stabilized (2-3 minutes). Remove cap and rinse sample bottle twice with sample.
3. Reduce flow. Fill a 250 mL sample bottle completely (leaving no airspace). Do not agitate the sample. Cap.

Shipping/Handling:

- Chlorine in aqueous solution is not stable, and the chlorine content of the sample, particularly weak concentrations, will decrease rapidly. Do not agitate the sample. Begin chlorine determination immediately after sampling.
- Protect sample from sunlight or strong artificial light.

EPA Approved Analytical Methods:

Methods approved for analysis of chlorine (free, combined, total).

- **SM 4500-Cl D.** Amperometric Titration Method
- **SM 4500-Cl F.** DPD Ferrous Titrimetric Method
- **SM 4500-Cl G.** DPD Colorimetric Method
- **ASTM D 1253-86.**

Additional methods approved for analysis of chlorine (total).

- **SM 4500-Cl E.** Low-level Amperometric Titration Method
- **SM 4500-Cl I.** Iodometric Electrode Technique

Additional method approved for analysis of chlorine (free).

- **SM 4500-Cl H.** Syringaldazine (FACTS) Method

Chlorine Dioxide — *Maximum holding time: Analyze immediately*

Chlorine dioxide, ClO_2, is applied to water supplies for taste and odor control, oxidation of soluble iron and manganese, and for disinfection purposes.

ClO_2, chlorine, chlorite, and hypochlorite are not easily distinguished by some methods. The amperometric method (E) can distinguish the various chlorine compounds with good accuracy and precision, but requires specialized equipment and considerable analytical skill. The DPD method (D) has the advantages of a relatively easy-to-perform colorimetric test with the ability to distinguish between ClO_2 and some forms of chlorine. This technique is not as accurate as the amperometric method, but should yield results adequate for many common applications.

Sampling Equipment:

Container: 250 mL plastic bottle.
Preservative: None. Analyze sample immediately.
Other:

- Field log book
- Labels/marker
- Gloves and goggles

Sample Collection Procedure:

1. Remove aerator and screen.
2. Turn on cold water tap and allow system to flush until water temperature has stabilized (2-3 minutes). Remove cap and rinse sample bottle twice with sample.
3. Reduce flow. Fill a 250 mL sample bottle completely (leaving no airspace). Do not agitate the sample. Cap.

Shipping/Handling:

- Determine ClO_2 promptly after collecting the sample. ClO_2 is volatile and will vaporize easily from aqueous solutions. Do not aerate or mix.
- Protect sample from sunlight or strong artificial light.
- Minimize ClO_2 losses by analyzing the sample, immediately, at the site of sample collection.

EPA Approved Analytical Methods:

- **SM 4500-ClO_2 D.** DPD Method
- **SM 4500-ClO_2 E.** Amperometric Method II

Total Trihalomethanes (TTHM) — *Maximum holding time: 14 days*

Toxicological studies indicate that organic compounds may react with disinfectants in drinking water to produce potentially toxic and carcinogenic compounds, often referred to as disinfection byproducts. Some of these disinfection byproducts are called total trihalomethanes (TTHM). TTHM is the sum of the measured concentrations of chloroform, bromodichloromethane, dibromochloromethane, and bromoform.

Sampling Equipment:

- **Method Specific Equipment:**

For EPA Methods 502.2 and 524.2

Container: (2) amber or clear glass vials with teflon lined septa, capacity 40-120 mL.
Note: If samples contain residual chlorine, use vials pre-fixed with 3 mg of sodium thiosulfate ($Na_2S_2O_3$) or 25 mg ascorbic acid per 40 mL sample for dechlorination.

Preservative: Add 0.5 mL (≈ 2 drops) 1:1 hydrochloric acid (HCl) per 40 mL sample for pH adjustment to pH <2.

For EPA Method 551.1

Container: (2) amber or clear glass vials with teflon lined septa, capacity 60 mL.

Preservative and dechlorinating agent:
Vials should be pre-fixed with a homogenous phosphate buffer/dechlorinating agent mixture as follows. Add 1 gm phosphate buffer and ammonium chloride (NH_4Cl) or sodium sulfite (Na_2SO_3) mixture/60 mL sample. (Mixture consists of 1 part Na_2HPO_4, 99 parts KH_2PO_4 and 0.6 parts NH_4Cl or Na_2SO_3. 1gm/60mL sample results in a pH of 4.8-5.5 and 0.1 mg NH_4Cl or Na_2SO_3/mL of sample.)

Other Equipment:

- Field log book
- Labels/marker
- Tamper-evident seals
- Cooler/ice
- Gloves and goggles
- Organic-free water for blanks
- pH test strip paper
- Field equipment for analysis of chlorine residual

Sample Collection Procedure:

- **Method Specific Information:**

For EPA Method 502.2 and 524.2

1. Remove aerator and screen.
2. Turn on cold water tap and allow system to flush until water temperature has stabilized (2-3 minutes). Reduce flow (to thickness of pencil).
3. Remove cap. Fill vial ¾ full.
4. Allow the dechlorinating agent (sodium thiosulfate or ascorbic acid) to dissolve. **Note:** Samples must be dechlorinated prior to acidification.
5. Add 1:1 HCl to the sample.
   Note: pH must be 1<pH<2. If you suspect volume of HCl is not sufficient to lower pH to within this range (i.e., water has high alkalinity or pH), check the pH (using pH test strip paper) of an equal volume of acidified sample.
6. Continue to fill vial completely with sample (creating a meniscus), but do not overflow/flush out preservatives.
7. Cap. Invert repeatedly for 1 minute to mix. Check for air bubbles (sample must be headspace free). If air bubbles are present, use the cap to carefully add more sample to the vial.
8. Immediately fill second vial with sample (duplicate sample) using the same procedure.

Note: Field or trip blanks must be handled along with each sample set. Contact your laboratory for information about QC samples.

For EPA Method 551.1

1. Remove aerator and screen.
2. Turn on cold water tap and allow system to flush until water temperature has stabilized (2-3 minutes). Reduce flow (to thickness of pencil).
3. Remove cap. Fill vial completely with sample (creating a meniscus), but do not overflow/flush out preservatives.
4. Cap. Invert repeatedly for 1 minute to mix. Check for air bubbles (sample must be headspace free). If air bubbles are present, use the cap to carefully add more sample to the vial.
5. Immediately fill second vial with sample (duplicate sample) using the same procedure.

Note: Field or trip blanks must be handled along with each sample set. Contact your laboratory for information about QC samples.

Shipping/Handling:

- Ice or refrigerate samples ≤4°C from time of collection to analysis.

EPA Approved Analytical Method:

- **EPA Method 502.2.** Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series
- **EPA Method 524.2.** Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry
- **EPA Method 551.1.** Determination of Chlorination Disinfection Byproducts, Chlorinated Solvents, and Halogenated Pesticides/Herbicides in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography with Electron-Capture Detection

Haloacetic Acids (HAA5)

Maximum holding times:

EPA 552.1: *28 days; analyze within 48 hours of extraction.*

EPA 552.2: *14 days; analyze within 7 days of extraction at 4°C or within 14 days at ≤ -10°C.*

SM 6251 B: *9 days; analyze within 21 days of extraction at -11°C.*

The haloacetic acids are formed by the chlorination of natural organic (humic and fulvic) matter. Utilities using chlorine as a water disinfectant generate haloacetic acids, usually as the second most prevalent group of known disinfection byproducts; the primary group formed is usually the trihalomethanes. Toxicological studies indicate that dichloroacetic acid and trichloroacetic acid are animal carcinogens. The USEPA has proposed a maximum level for the sum of five haloacetic acids, and requires utilities to monitor drinking water for specified haloacetic acids.

Sampling Equipment:

- **Method Specific Equipment**

For EPA Method 552.1

Container: (2) amber glass bottles with teflon lined septa, minimum capacity 250 mL.
Note: If samples contain residual chlorine, use bottles pre-fixed with *ammonium chloride (NH_4Cl) to produce a concentration of 100 mg/L (i.e., 0.1 mg/mL sample) for dechlorination.

For EPA Method 552.2

Container: (2) amber glass bottles with teflon lined septa, minimum capacity 50 mL.
Note: If samples contain residual chlorine, use bottles pre-fixed with *ammonium chloride (NH_4Cl) to produce a concentration of 100 mg/L (i.e., for a 50 mL sample, add 5 mg of NH_4Cl) for dechlorination.

For Standard Method 6251 B

Container: (2) glass vials with teflon lined septa, capacity 40 or 60 mL.
Note: If samples contain residual chlorine, add dechlorinating agent to bottle before filling (65 mg *ammonium chloride (NH_4Cl) – bake overnight at >100°C to eliminate contaminants).

**Although referenced as a dechlorinating agent, ammonium chloride converts free chlorine to monochloramine (combined chlorine)*.

Other Equipment:

- Field log book
- Labels/marker
- Tamper-evident seals
- Cooler/ice
- Gloves and goggles
- Organic-free water for blanks
- Field equipment for analysis of chlorine residual

Sample Collection Procedure:

1. Remove aerator and screen.
2. Turn on cold water tap and allow system to flush until water temperature has stabilized (2-3 minutes). Reduce flow (to thickness of pencil).
3. Remove cap. Fill bottle completely with sample (creating a meniscus), but do not overflow/flush out preservative.
4. Cap. Invert repeatedly for 1 minute to mix. Check for air bubbles (sample must be headspace free). If air bubbles are present, use the cap to carefully add more sample to the vial.
5. Immediately fill second bottle with sample (duplicate sample) using the same procedure.

Note: Contact your laboratory for information about QC samples.

Shipping/Handling:

- Ice or refrigerate samples ≤4°C from time of collection to analysis.
- Protect samples from light.

EPA Approved Analytical Methods:

- **EPA Method 552.1.** Determination of Haloacetic Acids and Dalapon in Drinking Water by Ion-Exchange Liquid-Solid Extraction and Gas Chromatography with an Electron Capture Detector.
- **EPA Method 552.2.** Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Extraction, Derivatization and Gas Chromatography with Electron Capture Detection.
- **SM 6251 B.** Determination of Haloacetic Acids and Trichlorophenol in Drinking Water by Micro Liquid-Liquid Extraction Gas Chromatographic Method.

Bromate — *Maximum holding time: 28 days*

The DBPR requires systems that use ozone to monitor for bromate. In addition, these systems will need to monitor for bromide, if they wish to qualify for reduced bromate monitoring. Bromate is one of the principal byproducts of ozonation in bromide-containing source waters. EPA considers bromate to be a probable or likely human carcinogen.

Sampling Equipment:

Container: Bottles, plastic or glass, capacity 30-250 mL.
Preservative: Use bottles pre-fixed with 50 mg/L ethylenediamine (EDA) solution (i.e., add 0.5 mL EDA to a 1 liter sample).

Other:

- Field log book
- Labels/marker
- Tamper-evident seals
- Cooler/ice
- Gloves and goggles

Sample Collection Procedure:

1. Remove aerator & screen.
2. Turn on cold water tap and allow system to flush until water temperature has stabilized (2-3 minutes).
3. Fill sample bottle, but do not overflow/ flush out preservative.
4. Cap. Invert several times to mix.

Shipping/Handling:

- Ice or refrigerate samples ≤4°C from time of collection to analysis.

EPA Approved Analytical Method:

EPA Method 300.1. Determination of Inorganic Anions in Drinking Water by Ion Chromatography

Bromide — *Maximum holding time: 28 days*

The DBPR requires systems that use ozone to monitor for bromate. In addition, these systems will need to monitor for Bromide, if they wish to qualify for reduced bromate monitoring. Bromate is one of the principal byproducts of ozonation in bromide-containing source waters. EPA considers bromate to be a probable or likely human carcinogen.

Sampling Equipment:

Container: Bottles, plastic or glass, capacity 30-250 mL.
Preservative: None required.
Note: Bromide can be analyzed in a sample matrix which has been preserved for bromate analysis with 50 mg/L EDA.

Other:

- Field log book
- Labels/marker
- Tamper-evident seals
- Cooler/ice
- Gloves and goggles

Sample Collection Procedure:

1. Remove aerator & screen.
2. Turn on cold water tap and allow system to flush until water temperature has stabilized (2-3 minutes).
3. Remove cap and rinse sample bottle twice with sample.
4. Fill sample bottle completely.
5. Cap.

Shipping/Handling:

- Ice or refrigerate samples ≤4°C from time of collection to analysis.

EPA Approved Analytical Methods:

EPA Method 300.0. Determination of Inorganic Anions by Ion Chromatography

EPA Method 300.1. Determination of Inorganic Anions in Drinking Water by Ion Chromatography

Chlorite

Max holding time: Analyze immediately(4500-ClO_2 E) or add EDA and analyze within 14 days (300.0 and 300.1)

The DBPR requires systems using chlorine dioxide to monitor for chlorite. Chlorine dioxide is rapidly reduced to chlorite. Chlorite has been shown to cause adverse reproductive or developmental effects in laboratory animals.

Note: A certified laboratory must analyze the monthly chlorite distribution samples, collected for compliance with the DBPR, using EPA Method 300.0 or 300.1. Routine, daily chlorite samples taken at the entry point to the distribution system may be analyzed immediately, by an approved party, using SM 4500-ClO_2 E.

Sampling Equipment:

- **Method Specific Equipment**

For EPA Method 300.0 and 300.1

Container: Bottles, opaque high-density polyethylene (HDPE), or amber glass, capacity 30–250 mL.
Preservative: Add 50 mg/L EDA (i.e., add 0.5 mL EDA to a 1 liter sample)
Equipment for Sparging Process:
Compressed inert gas (i.e., helium, argon, or nitrogen)
Flexible tubing. Gas source is attached at one end and the other end is attached to a disposable glass pipette.

For Standard Method 4500-ClO_2 E

Container: Glass or plastic bottle.
Preservative: None.
Sample Tap: Should be equipped with a flexible sample line that is small enough to fit inside the sample bottle and long enough to reach the bottom of the sample bottle.

Other:

- Field log book
- Labels/marker
- Tamper-evident seals
- Cooler/ice
- Gloves and goggles
- Field equipment for analysis of chlorine dioxide residual

Sample Collection Procedure:

- **Method Specific Information**

For EPA Method 300.0 and 300.1

1. Remove aerator & screen.
2. Turn on cold water tap and allow system to flush until water temperature has stabilized (2-3 minutes).
3. Measure and record chlorine dioxide residual.
4. Remove cap and rinse sample bottle twice with sample.
5. Fill sample bottle ¾ full.
6. If chlorine dioxide residual is present, sparge the sample with inert gas prior to the addition of EDA. To sparge the sample, place the tip of a disposable pipette at the bottom of the sample bottle and bubble the inert gas through the sample until there is no chlorine dioxide residual (≈10 minutes).
7. Add a sufficient volume of the EDA preservative such that the final concentration is 50 mg/L EDA in the sample (i.e., add 0.5 mL EDA to a 1 liter sample).
8. Cap. Invert several times to mix.

For SM 4500-ClO_2 E

1. Remove aerator and screen. Attach a flexible sample line.
2. Turn on cold water tap and allow system to flush until water temperature has stabilized (2-3 minutes).
3. Remove cap and rinse bottle with sample.
4. Place flexible sample line into the bottom of the bottle.
5. Fill sample bottle completely, allowing it to overflow several container volumes.
6. Slowly remove sample line.
7. Cap bottle immediately with minimum headspace.
8. Analyze sample immediately.

Shipping/Handling:

- For EPA methods 300.0 and 300.1, ice or refrigerate samples ≤4°C from time of collection to analysis and protect samples from light.

- For SM 4500-ClO_2E, analyze samples immediately.

EPA Approved Analytical Methods:

EPA Method 300.0. Determination of Inorganic Anions by Ion Chromatography

EPA Method 300.1. Determination of Inorganic Anions in Drinking Water by Ion Chromatography

SM 4500-ClO2 E. Amperometric Method II

Total Organic Carbon (TOC) — *Maximum holding time: 28 days*

The organic carbon in water is composed of a variety of organic compounds in various oxidation states. Toxicological studies indicate that, for drinking waters in particular, organic compounds may react with disinfectants to produce potentially toxic and carcinogenic compounds, often referred to as disinfection byproducts. Conventional filtration plants are required to monitor raw and filtered water to determine TOC levels and % removal.

Sampling Equipment:

Container: (2) organic-free amber glass bottles with teflon lined septa. Use screw caps with thick silicone rubber-backed TFE septa with open ring to produce a positive seal. Minimum capacity 40 mL.

Preservative: Use bottles pre-fixed with sulfuric acid (H_2SO_4) or phosphoric acid (H_3PO_4) for pH adjustment as follows: (i.e., ≈0.5 mL 10 % sulfuric acid/40 mL sample).

Other:

- Field log book
- Labels/marker
- Tamper-evident seals
- Cooler/ice
- Gloves and goggles
- Organic-free water for blanks

Sample Collection Procedure:

1. Remove aerator and screen.
2. Turn on cold water tap and allow system to flush until water temperature has stabilized (2-3 minutes). Reduce flow (to thickness of a pencil).
3. Remove cap and fill sample bottle completely (creating a meniscus), but do not overflow/flush out preservative.
4. Cap. Invert several times to mix. Check for air bubbles (sample should be head-space free). If air bubbles are present, use the cap to carefully add more sample to the vial.
5. Immediately fill second bottle with sample (duplicate sample) using the same procedure.

Note: Contact your laboratory for information about QC samples.

Additional Quality Control (QC) Procedures:

The federal DBPR (40 CFR 141.131(d)(3)) requires certain QC procedures for TOC analyses in addition to those contained in the method descriptions. These additional QC steps are designed to increase the integrity of the analysis and have been found to be effective in data collection under the ICR.

1. Filtration of samples prior to TOC analysis is not permitted, as this could result in removal of organic carbon.
2. Where turbidity interferes with TOC analysis, samples should be homogenized and, if necessary, diluted with organic-free reagent water.
3. TOC samples must either be analyzed or must be acidified to achieve pH less than 2.0 by minimal addition of phosphoric or sulfuric acid as soon as practical after sampling, not to exceed 24 hours.
4. Samples must be analyzed within 28 days.

In addition, EPA issued the following guidance for TOC analysis. There is a concern that inorganic carbon in water samples may impact the reliability of TOC analyses. EPA's Office of Research and Development (ORD) confirmed that inorganic carbon not properly removed from water samples prior to TOC analyses my bias results. Inorganic carbon (i.e., carbon dioxide, carbonate, bicarbonate) may be removed by sparging (i.e., air-stripping). Standard Methods specifies that inorganic carbon needs to be removed prior to analysis but it did not describe a procedure, nor did it specifically outline QA/QC protocols. In order to clarify how inorganic carbon should be removed and establish baseline QC protocols, ORD is developing a new analytical method. For additional information, please contact Ed Moriarty at (202) 564-3864 or by email at moriarty.Edward@epa.gov.

Shipping/Handling:

- Ice or refrigerate samples ≤4°C from time of collection to analysis.
- Protect samples from light.

Analytical Methods:

- **SM 5310 B.** Infrared Method.
- **SM 5310 C.** Persulfate-Ultraviolet or Oxidation Method.
- **SM 5310 D.** Wet-Oxidation Method.

Specific Ultraviolet Absorbance (SUVA)

The DBPR establishes Specific Ultraviolet Absorbance (SUVA) as an alternative criterion for demonstrating compliance with TOC removal requirements.

SUVA is a calculated parameter defined as the UV absorption at 254 nm (UV_{254}) (measured as m^{-1}) divided by the DOC concentration (measured as mg/L). If the UV absorption is first determined in units of cm^{-1}, the SUVA equation is multiplied by 100 to convert to m^{-1}, as shown below:

$$\textbf{SUVA} = 100\ (cm/m) \times [UV_{254}(cm^{-1})/DOC\ (mg/L)]$$

Waters with low SUVA values contain primarily non-humic matter and are not amenable to enhanced coagulation. Systems are not required to perform enhanced coagulation or enhanced softening if the raw water SUVA is ≤2.0 L/mg-m.

Note: Two separate analytical methods are necessary to make this determination: UV_{254} and DOC. Refer to the following procedures.

Ultraviolet Absorption Method (UV_{254})

Maximum holding time: 48 hours

Some organic compounds commonly found in water, such as lignin, tannin, humic substances, and various aromatic compounds, strongly absorb ultraviolet (UV) radiation. UV absorption is a useful surrogate measure of selected organic constituents. A strong correlation may exist between UV absorption and organic carbon content, color, and precursors of trihalomethanes (THMs) and other disinfection byproducts.

This method should be used as an indication of the aggregate concentration of UV-absorbing organic constituents.

Sampling Equipment:

Container: (2) Amber glass bottles with teflon lined septa, capacity varies with lab.

Preservative: Ice or refrigerate samples ≤4°C. No further preservation needed at time of collection. However, your lab will need to filter the sample for analysis within 48 hours.

Other:

- Field log book
- Labels/marker
- Tamper-evident seals
- Cooler/ice
- Gloves and goggles

Sample Collection Procedure:

1. Remove aerator & screen.
2. Turn on cold water tap and allow system to flush until water temperature has stabilized (2-3 minutes). Reduce flow (to thickness of a pencil).
3. Remove cap and rinse bottle with sample.
4. Fill sample bottle. Cap.
5. Immediately fill second bottle with sample (duplicate sample) using the same procedure.

Additional Quality Control (QC) Procedures:

The federal DBPR (40 CFR 141.131(d)(4)) contains QC steps for the SUVA analyses that are required in addition to those mandated in the method descriptions.

1. **Sample acquisition:** DOC and UV_{254} samples used to determine a SUVA value must be taken at the same time and at the same location. SUVA must be determined on water prior to the addition of disinfectants/oxidants.
2. **Sample preservation:** The pH of UV_{254} samples may not be adjusted. Ice or refrigerate samples ≤4°C from time of collection to analysis.
3. **Holding times:** UV_{254} samples must be analyzed as soon as practical after sampling, not to exceed 48 hours.

Shipping/Handling:

- Ice or refrigerate samples ≤4°C from time of collection to analysis.
- Protect samples from light.

EPA Approved Analytical Method:

SM 5910 B. Ultraviolet Absorption Method.

Dissolved Organic Carbon (DOC) *Maximum holding time: 28 days*

DOC measurements are performed using the same analytical techniques used to measure TOC. However, samples for DOC measurement must be vacuum-filtered or pressure filtered through a 0.45 um pore size filter in the laboratory, prior to analysis. To prevent contamination, the membrane filter must be washed with reagent-grade water. Water passed through the filter prior to sample filtration must be saved and used as a filtered blank. DOC samples must be acidified to a pH <2.0 by adding phosphoric or sulfuric acid as soon as possible, but not to exceed 48 hours, after sampling and filtration.

Sampling Equipment:

Container: (2) organic-free amber glass bottles with teflon lined septa. Use screw caps with thick silicone rubber-backed TFE septa with open ring to produce a positive seal. Minimum capacity 40 mL.

Preservative: None required at time of collection. However, your lab will need to filter and preserve [with sulfuric acid (H_2SO_4) or phosphoric acid (H_3PO_4) to a pH <2 (i.e., ≈0.5 mL 10 % sulfuric acid/40 mL sample] the sample for DOC analysis within 48 hours.

Other:

- Field log book
- Labels/marker
- Tamper-evident seals
- Cooler/ice
- Gloves and goggles
- Organic-free water for blanks

Sample Collection Procedure:

1. Remove aerator and screen.
2. Turn on cold water tap and allow system to flush until water temperature has stabilized (2-3 minutes). Reduce flow (to thickness of a pencil).
3. Remove cap and rinse bottle with sample.
4. Fill sample bottle completely (creating a meniscus). Sample should be head-space-free with no air bubbles.
5. Cap.
6. Immediately fill second bottle with sample (duplicate sample) using the same procedure.

Additional Quality Control (QC) Procedures:

The federal DBPR (40 CFR 141.131(d)(4)) contains QC steps for DOC analyses that are required in addition to those mandated in the method descriptions.

1. **Sample acquisition:** DOC and UV_{254} samples used to determine a SUVA value must be taken at the same time and at the same location. SUVA must be determined on water prior to the addition of disinfectants/oxidants.
2. **Sample preservation:** DOC samples must either be analyzed or must be acidified to achieve pH less than 2.0 by minimal addition of phosphoric or sulfuric acid as soon as practical after sampling, not to exceed 48 hours.
3. **Holding times:** DOC samples must be analyzed within 28 days of sampling.

Shipping/Handling:

- Ice or refrigerate samples ≤4°C from time of collection to analysis.
- Protect samples from light.

EPA Approved Analytical Methods:

- **SM 5310 B.** High-Temperature Combustion Method
- **SM 5310 C.** Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method
- **SM 5310 D.** Wet-Oxidation Method

Alkalinity — *Maximum holding time: ASAP, not to exceed 14 days*

Alkalinity of a water is its acid-neutralizing capacity. Total alkalinity is measured by titration of the sample to an electrochemically determined endpoint (i.e., pH 4.5). Alkalinity is reported in mg/L as calcium carbonate ($CaCO_3$). The methods attribute the entire alkalinity concentration to the sum of carbonate, bicarbonate, and hydroxide concentrations. The sample pH of the source water where the sample was collected must be recorded. Care must be used in sampling and storage.

Sampling Equipment:

Container: Polyethylene or borosilicate glass bottle (not acid washed), minimum capacity 200 mL.

Preservative: None.

Other:

- Field log book
- Labels/marker
- Tamper-evident seals
- Cooler/ice
- Gloves and goggles
- Field test equipment for measuring pH

Sample Collection Procedures:

1. Remove aerator and screen.
2. Turn on cold water tap and allow system to flush until water temperature has stabilized (2-3 minutes).
3. Measure and record pH of sample.
4. Reduce flow (to thickness of pencil).
5. Remove cap and rinse bottle with sample.
6. Fill sample bottle completely to minimize headspace. Avoid sample agitation and prolonged exposure to air.
7. Cap.

Shipping/Handling:

- Analyze sample immediately or ice/refrigerate sample ≤4°C from time of collection to analysis.

EPA Approved Analytical Methods:

SM 2320 B. Titration Method
ASTM D-1067-92B. Titration Method.
USGS I-1030-85. Titration Method.

pH — ***Maximum holding time: Analyze immediately***

Measurement of pH is one of the most important and frequently used tests in water chemistry. Practically every phase of water treatment is pH-dependent.

The typical electrometric apparatus (pH meter) consists of a potentiometer, a glass electrode, a reference electrode, and a temperature-compensating device. When the electrodes are immersed in the sample solution, a circuit is completed through the potentiometer; the potentiometer measurement is used to determine the activity of the hydrogen ions. pH must be analyzed immediately, in the field.

Sampling Equipment:

Container: Plastic or glass bottle, capacity ≈100 mL.
Preservation: None. Analyze sample immediately.
Other: Field log book

Sample Collection Procedures:

1. Remove aerator and screen.
2. Turn on cold water tap and allow system to flush until water temperature has stabilized (2-3 minutes).
3. Remove cap and rinse bottle with sample.
4. Fill sample bottle completely to minimize headspace. Avoid sample agitation and prolonged exposure to air.
5. Cap.

Shipping/Handling:

- Analyze sample immediately, in the field.

EPA Approved Analytical Methods:

EPA Method 150.1. Electrometric Method
EPA Method 150.2. pH, Continuous Monitoring (Electrometric) Method
SM 4500-H^+B. Electrometric Method
ASTM D1293-84. Standard Test Methods for pH of Water

Magnesium Hardness — *Maximum holding time: 6 months*

Precipitative softening systems monitoring to meet alternative performance criteria (magnesium hardness removal greater than or equal to 10 mg/L as $CaCO_3$) will need to perform analyses for magnesium.

Sampling Equipment:

Container: Plastic or glass bottle, capacity 250 - 500 mL.
Preservation: Add 3 - 5 mL 1:1 Nitric Acid (HNO_3) per liter of sample for pH adjustment.

Other:

- Field log book
- Labels/marker
- Tamper-evident seals
- Cooler/ice
- Gloves and goggles
- pH test strip paper

Sample Collection Procedures:

1. Remove aerator and screen.
2. Turn on cold water tap and allow system to flush until water temperature has stabilized (2-3 minutes).
3. Remove cap and rinse bottle with sample.
4. Fill sample bottle to neck (leave headspace). Add 1:1 HNO_3 to sample to adjust pH < 2.
5. Cap. Invert several times to mix.

Shipping/Handling:

- Ice or refrigerate samples at $\leq 4°C$ from time of collection until analysis.

EPA Approved Analytical Methods:

EPA Method 200.7. Inductively Coupled Plasma Method
SM 3111 B. Atomic Absorption Method
SM 3120 B. Inductively Coupled Plasma
SM 3500-Mg E. Complexation Titrimetric Method
ASTM D 511-93 A. Complexation Titrimetric Method
ASTM D 511-93 B. Atomic Absorption Method

References:

ASTM Methods D 1067-92B, D 1253-86, D 1293-84, D 511-93A and D 511-93B are in Annual Book of ASTM Standards, Vols. 11.01 and 11.02, ASTM, 1994 and 1996.

EPA Methods 150.1 and 150.2 are in Methods for Chemical Analysis of Water and Wastes, USEPA, 1983, EPA 600/4-79/020.

EPA Method 200.7 is in Methods for the Determination of Metals in Environmental Samples – Supplement I, USEPA, 1994, EPA 600/R-94-111.

EPA Method 300.0 is in Methods for the Determination of Inorganic Substances in Environmental Samples, USEPA, August 1993, EPA 600/R-93/100.

EPA Method 300.1 is titled USEPA Method 300.1, Determination of Inorganic Anions in Drinking Water by Ion Chromatography, Revision 1.0, USEPA, 1997, EPA 600/R-98/118.

EPA Methods 502.2, 524.2, 551.1 and 552.2 are in Methods for the Determination of Organic Compounds in Drinking Water – Supplement III, USEPA, August 1995, EPA/600/R-95/131.

EPA Method 552.1 is in Methods for the Determination of Organic Compounds in Drinking Water – Supplement II, USEPA, August 1992, EPA/600/R-92/129.

Method I-1030-85 is in Techniques of Water Resources Investigation of the U.S. Geological Survey, Book 5, Chapter A-1, 3rd ed., 1989.

Standard Methods 2320 B, 3111 B, 3120 B, 3500-Mg E and 4500-H^+ B are in the 18th, 19th and 20th editions of Standard Methods for the Examination of Water and Wastewater, APHA, 1992, 1995 and 1998.

Standard Methods 4500-Cl D, 4500-Cl E, 4500-Cl F, 4500-Cl G, 4500-Cl H, 4500-Cl I, 4500-ClO_2 D, 4500-ClO_2 E, 6251 B and 5910 B are in Standard Methods for the Examination of Water and Wastewater, 19th ed., APHA, 1995.

Standard Methods 5310 B, 5310 C and 5310 D are in the Supplement to the 19th Edition of Standard Methods for the Examination of Water and Wastewater, APHA, 1996.

Alternative Disinfectants and Oxidants Guidance Manual, USEPA, 1999, EPA 815-R-99-014.

Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual, USEPA, 1999, EPA 815-R-99-012.