

Surface Water Protection Preservation and Hold Time Table

Aqueous Samples				
Listed below is information on the collection and preservation of samples. The amount of sample listed is for routine conditions. If you suspect that unusual conditions or interferences exist, please submit double the amount of sample. Excluding purgeable organics and sulfide, a one-half inch air space should be left in all bottles to allow for mixing before analysis. The parameters are listed in the same order as they appear on the DM-1 form.				
Parameter ⁽¹⁾	Minimum Required Volume	Container ⁽¹³⁾	Preservation ⁽²¹⁾	Maximum Hold Time ⁽²²⁾
BOD, 5-day	1 liter	P	Cool, ≤6°C	48 hours ⁽²⁾
CBOD, 5-day	1 liter	P	Cool, ≤6°C	48 hours ⁽²⁾
COD	200 mL	P (Disposable)	Cool, ≤6°C, 25% H ₂ SO ₄ to pH<2	28 days
Coliform (Total, Fecal, <i>E. coli</i> and Enterococci)	250 mL each	P (Sterile) (3)	Cool, <10°C, 0.008% Na ₂ S ₂ O ₃ (0.1 mL 10% Na ₂ S ₂ O ₃ per 125 mL) and 15% EDTA ⁽³⁾	6 hours ⁽⁴⁾
Residue (TS, TSS) ⁽¹⁸⁾	500 mL each	P (Disposable)	Cool, ≤6°C	7 days
Total Dissolved Solids (TDS)	500 mL each	P (Disposable)	Cool, ≤6°C	7 days
pH ⁽⁵⁾	Inappropriate for laboratory analysis			Immediate - field measurement
A. Acidity ⁽¹⁸⁾	200 mL	P (Disposable)	Cool, ≤6°C	14 days
A. Alkalinity ⁽¹⁸⁾	200 mL	P (Disposable)	Cool, ≤6°C	14 days
A. Bicarbonate	combined w/above	Request on Field Sheet and submit alkalinity sample.		
A. Carbonate	combined w/above	Request on Field Sheet and submit alkalinity sample.		
TOC	200 mL	P (Disposable)	Cool, ≤6°C, H ₃ PO ₄ to pH<2	28 days
DOC	200 mL - A Field Blank must accompany all DOC samples ⁽²⁶⁾	P (Disposable)	Field filter using 0.45 µm filter, Cool, ≤6°C, H ₃ PO ₄ to pH<2	28 days
Turbidity	200 mL	P (Disposable)	Cool, ≤6°C	48 hours ⁽²⁾
C. Chloride	500 mL x 1	P (Disposable)	Cool, ≤6°C when combined with SO ₄ - no thermal preservation required if requesting chloride only	28 days
C. Fluoride	combined w/above	P (Disposable)	Cool, ≤6°C when combined with SO ₄ - no thermal preservation required if requesting fluoride only	28 days
C. Sulfate	combined w/above	P (Disposable)	Cool, ≤6°C	28 days
Chlorophyll a ⁽¹⁰⁾	500 mL	P (Brown, wide-mouth bottle)	Cool, ≤6°C ^{(12) (24)}	24 hours ^{(12) (24)}
Color	200 mL	P (Disposable)	Cool, ≤6°C	48 hours ⁽²⁾
Chromium, Hexavalent	200 mL	P (Disposable)	Cool, ≤6°C	24 hours (notify lab of collection)
Cyanide, Total	2 liters (two 1-liter bottles)	P	Cool, ≤6°C, 0.6 g ascorbic acid ⁽⁶⁾ , 6N NaOH to pH>12	14 days ⁽¹⁹⁾
Formaldehyde	500 mL	P (Disposable)	Cool, ≤6°C	N/A
HEM: Oil and Grease	2 liters (two 1-liter bottles) ⁽¹⁷⁾	G (Wide-mouth quart jar, Teflon-lined cap)	Cool, ≤6°C, 6N H ₂ SO ₄ to pH<2	28 days
Total Hardness (request by checking Ca and Mg on field sheet - can be part of metals suite) Total Hardness (mg CaCO₃/L) = 2.497 [Ca, mg/L] + 4.118 [Mg, mg/L]	500 mL	P (Disposable)	1+1 HNO ₃ to pH<2	6 months
MBAS	500 mL	P (Disposable)	Cool, ≤6°C	48 hours ⁽²⁾ (notify lab of collection)

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Parameter ⁽¹⁾	Minimum Required Volume	Container ⁽¹³⁾	Preservation ⁽²¹⁾	Maximum Hold Time ⁽²²⁾
Phenols, Total Recoverable	2 liters (two 1-liter bottles)	G (Phenol bottle) only	Cool, ≤6°C, 1:1 H2SO4 to pH<2 (1 mL ferrous ammonium sulfate if sample contains oxidizer)	28 days
Sulfide	40 mL x 3 ⁽⁹⁾	G (40 mL VOA vials with Teflon-lined septum)	Cool, ≤6°C, add 0.1 mL 2N zinc acetate plus 6N NaOH to pH>9, leave NO headspace in the bottle	7 days
Specific Conductance	200 mL	P (Disposable)	Cool, ≤6°C	28 days
Tannin and Lignin	500 mL	P (Disposable)	Cool, ≤6°C	28 days
B. NH3 as N	500 mL x 1	P (Disposable)	Cool, ≤6°C, 25% H2SO4 to pH<2 ⁽⁷⁾ (0.008% Na2S2O3 if chlorine present) ⁽¹¹⁾	28 days
B. TKN as N	combined w/above	P (Disposable)	Cool, ≤6°C, 25% H2SO4 to pH<2 ⁽⁷⁾ (0.008% Na2S2O3 if chlorine present) ⁽¹¹⁾	28 days
B. NO3+NO2 as N	combined w/above (except when NH3 and TKN require dechlorination)	P (Disposable)	Cool, ≤6°C, 25% H2SO4 to pH<2 ⁽⁷⁾	28 days
B. TP, total as P	combined w/above (except when NH3 and TKN require dechlorination)	P (Disposable)	Cool, ≤6°C, 25% H2SO4 to pH<2 ⁽⁷⁾	28 days
TP, dissolved as P	200 mL	P (Disposable)	Filter immediately, Cool, ≤6°C, 25% H2SO4 to pH<2 ⁽⁷⁾	28 days
PO4 as P	200 mL	P (Disposable)	Filter immediately, Cool, ≤6°C	48 hours ⁽²⁾
NO2 as N	200 mL	P (Disposable)	Cool, ≤6°C	48 hours (notify lab of collection)
NO3 as N	200 mL + additional preserved sample for NO3+NO2	P (Disposable)	Cool, ≤6°C	48 hours (notify lab of collection)
C. Metals: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr (Total), Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sb, Sn, Se, Tl, V, Zn and Hg (20)	500 mL x 1	P (Disposable)	1+1 HNO3 to pH<2 ⁽²⁷⁾	6 months (28 days for Mercury)
Boron ⁽²⁵⁾	500 mL x 1	P (Disposable)	1+1 HNO3 to pH<2	6 months
EPA 1631 E Hg (trace level total Hg)	500 mL - A Field Blank must accompany each trace-level Hg sample	G (Borosilicate with Teflon-lined cap)	None required - Use "clean" sampling techniques as described in EPA Method 1669	28 days until preservation with BrCl ⁽²³⁾ Preserved samples are stable for up to 90 days from collection
Semivolatile Organics - Base/Neutral Acid Extractables	1 gal	G (Amber with Teflon-lined cap)	Cool, ≤6°C, 0.008% Na2S2O3 if chlorine present) ⁽¹¹⁾	7 days until extraction ⁽⁸⁾ 40 days after extraction
Pesticides/PCBs (OP Pest/OC Pest/ON Pest)	1 gal	G (Amber with Teflon-lined cap)	Cool, ≤6°C, 0.008% Na2S2O3 if chlorine present) ⁽¹¹⁾	7 days until extraction ^{(8) (15)} 40 days after extraction

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Parameter ⁽¹⁾	Minimum Required Volume	Container ⁽¹³⁾	Preservation ⁽²¹⁾	Maximum Hold Time ⁽²²⁾
Acid Herbicides	1 gal	G (Amber with Teflon-lined cap)	Cool, ≤6°C, 0.008% Na ₂ S ₂ O ₃ if chlorine present ⁽¹¹⁾	7 days until extraction ^{(8) (15)} 40 days after extraction
Purgeable (Volatile) Organics (VOA)	40 mL x 4 ⁽⁹⁾ - A Trip Blank (3 vials) must accompany all VOA samples	G (Teflon-lined septum)	Cool, ≤6°C, 0.008% Na ₂ S ₂ O ₃ if chlorine present ⁽¹¹⁾ , HCl to pH<2 ^{(14) (16)} , Leave no headspace in the bottle	14 days (7 days for aromatics only when unpreserved)
TPH Gasoline Range Organics and BTEX (aqueous)	40 mL x 4 ⁽⁹⁾ - A Trip Blank (3 vials) must accompany all VOA samples	G (Teflon-lined septum)	Cool, ≤6°C, 0.008% Na ₂ S ₂ O ₃ if chlorine present ⁽¹¹⁾ , HCl to pH<2 ^{(14) (16)} , Leave no headspace in the bottle	14 days
TPH Diesel Range Organics (aqueous)	1 gal	G (Teflon-lined cap)	Cool, ≤6°C	14 days until extraction 40 days after extraction

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Soil Samples

When submitting soil and sludge samples for analysis, a separate sample container must be collected for each of the analytical groups listed below:

Parameter/Analytical Group	Minimum Required Volume	Container ⁽¹³⁾	Preservation ⁽²¹⁾	Maximum Hold Time ⁽²²⁾
Oil and Grease	8 oz. jar	G, Teflon-lined cap	Cool, ≤6°C	refer to aqueous
Metals: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr (Total), Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sb, Sn, Se, Tl, V, Zn and Hg	8 oz. jar	G, Teflon-lined cap	Cool, ≤6°C	refer to aqueous
Pesticides/PCBs (OP Pest/OC Pest/ON Pest)	8 oz. jar	G, Teflon-lined cap	Cool, ≤6°C	14 days to extract; analyze within 40 days
Acid Herbicides	8 oz. jar	G, Teflon-lined cap	Cool, ≤6°C	14 days to extract; analyze within 40 days
Semivolatile Organics - Base/Neutral Acid Extractables	8 oz. jar	G, Teflon-lined cap	Cool, ≤6°C	14 days to extract; analyze within 40 days
Purgeable (Volatile) Organics (VOA)	4 oz. jar + trip blank	G, Teflon-lined cap or septum	Cool, ≤6°C	14 days
TPH Gasoline Range Organics and BTEX (aqueous)	4 oz. jar + trip blank	G, Teflon-lined cap or septum	Cool, ≤6°C	14 days
TPH Diesel Range Organics (aqueous)	8 oz. jar	G, Teflon-lined cap	Cool, ≤6°C	14 days to extract; analyze within 40 days

Footnotes

- (1) Determinations preceded by the same letter (i.e., A, B, C) may be submitted in the same bottle if the bottle contains enough sample. If not letter precedes a parameter, it must be submitted in a separate bottle.
- (2) 48 hours is the maximum holding time, however, samples should be submitted to the lab as soon as possible.
- (3) Use the 250 mL wide-mouth sterile plastic bottles for all samples. All bottles contain sodium thiosulfate and EDTA reagents.
- (4) Litigation samples must be delivered to the laboratory within 6 hours of sample collection.
- (5) It is recommended that pH analysis be performed on-site.
- (6) Add 0.6 g ascorbic acid only if the sample contains total residual chlorine.
- (7) Caution: Addition of excessive amounts of acid will interfere with the test procedures. The 2.0 mL of 25% H₂SO₄ per 500 mL sample should be added using a graduated or precise volume dispensing device. If no dispenser is available you may add exactly 40 drops of the 25% H₂SO₄. In most cases, the addition of 2.0 mL (~40 drops) of 25% H₂SO₄ to 500 mL of surface water will reduce the pH to <2, however, if the pH remains above 2, add acid dropwise with stirring until the pH is lowered to <2. For nutrient samples, the pH range of 1.5-2.0 is ideal to insure best possible recovery of analytes.
- (8) In a glass container, submit a small quantity of the pure compound of any suspected material.
- (9) Fill the bottle to overflowing and cap, leaving no air space (i.e., headspace).
- (10) EPA Method 445.0, Revision 1.2, September 1997 and EPA Method 446.0, Revision 1.2, September 1997.
- (11) Should only be used in the presence of residual chlorine. Add sodium thiosulfate or ascorbic acid (as appropriate) to the container first; fill at least half way before adding acid (if used). Adding 0.1 mL of a 10% solution of sodium thiosulfate (Na₂S₂O₃) per each 125 mL of sample is equivalent to 0.008% Na₂S₂O₃.
- (12) Used by the DWQ Chemistry Lab only at this time.
- (13) The container types listed are those commonly throughout the Department. Other container types may be acceptable. Please consult the laboratory about use of proper containers before deviating from those listed. P-plastic, G-glass, P (Disposable)-plastic disposable "juice" bottle.
- (14) Samples submitted for purgeable halocarbons only should not be acid-preserved.
- (15) Samples submitted for pesticide and acid herbicide analyses must be extracted within 72 hours of collection if the pH is not adjusted in the lab to a pH range of 5-9.
- (16) Samples submitted for purgeable aromatics receiving no pH adjustment must be analyzed within 7 days of collection.
- (17) The entire contents (i.e., whole volume sample) must be used for analysis.
- (18) Total Residue and Total Suspended Residue samples are to be shipped directly to the Central Laboratory for repacking and shipment to the Washington Regional Laboratory for analysis. Samples for these parameters collected in the Washington Region are sent directly to the WARO Lab.

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(19) Maximum hold time is 24 hours when sulfide is present. Optionally, all samples may be tested on-site with lead acetate paper before pH adjustment in order to determine if sulfide is present. If it is, it can be removed by the addition of CdNO₃ powder until a negative spot test is obtained.

(20) For dissolved metals, samples should be filtered immediately on-site before adding preservative.

(21) Sample preservation should be performed immediately upon collection. For composite samples, each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then the samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

(22) Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Collection times must allow for sample preparation and analytical set-up. Some samples may not be stable for the maximum time period given in the table. Collectors are obligated to hold the sample for as short a time as possible especially if knowledge exists showing that this is necessary to maintain sample stability.

(23) If samples are oxidized (digested) with bromine chloride (BrCl) in the same bottle that they are collected, then the preservation of the sample may be delayed up to twenty-eight days after the time of sample collection. The total hold time with proper preservation for EPA Method 1631 is ninety days after collection. Ref: EPA Method 1631, Revision E, Section 8.5.

(24) Samples are cooled to 4°C at the time of collection. Due to the limitations of filtering samples in the field, it is the DWQ Laboratory Section's policy to filter chlorophyll samples the day that the samples are received at the lab, not to exceed 24 hours from collection. Filters can be stored frozen in the dark for as long as 3 and 1/2 weeks without significant loss of chlorophyll a.

(25) You must write in "Boron" in one of the blank cells on the field sheet to request Boron analysis and submit a separate metals sample.

(26) A field filter blank should accompany all DOC samples. Samplers may obtain water for this purpose from the Central Laboratory just prior to each sampling event. On the field sheet, write "DIS" next to TOC to request DOC analysis. Complete a separate field sheet for the DOC filter blank.

(27) An aqueous metals sample may be collected and shipped without acid preservation, however, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. If the sample must be analyzed within 24 hours of collection, add the acid

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