

Ground Water and UST Samples – Containers, Preservation, Hold Times Table
 NCDWR-Water Sciences Section-Chemistry Laboratory

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North Carolina Division of Water Resources, Water Sciences Section – Chemistry Laboratory

Reference: 40 CFR Part 136.3 Table II

Listed below is information to be used in the collection and preservation of ground water samples (including for UST).
 Filtered samples are requested for some parameters as recommended by the USGS manual.

- **Excluding volatile organics and sulfide**, a one-half inch air space should be left in all bottles to allow for mixing before analysis.
- **When submitting a filtered sample, write "DIS" (for dissolved) in the box beside the parameter(s) on the field sheet**

- **Samples must be shipped to the Laboratory as soon as possible after collection.**

Parameter ²	Minimum Required Volume	Container ^{1,14} P-Plastic G-Glass	Preservation ¹⁸	Maximum Holding Time ¹⁹
Microbiology Unit Parameters:				
Alkalinity • includes bicarbonate & carbonate	200 ml	P (disposable)	Cool ≤6°C ²¹	14 days
BOD 5-day	1 liter	P	Cool ≤6°C ²¹	48 hours ⁶ <i>(notify lab)</i>
CBOD 5-day	1 liter	P	Cool ≤6°C ²¹	48 hours ⁶ <i>(notify lab)</i>
<u>Coliform:</u> Fecal, Total	250 ml (each) <i>(cannot be combined)</i>	P (sterile) ⁷	Cool ≤6°C ²¹ 0.008% Na ₂ S ₂ O ₃ (0.1ml 10% Na ₂ S ₂ O ₃ /125 ml) and 15% EDTA ⁷	6 hours ⁸
Specific Conductance	200 ml	P (disposable)	Cool ≤6°C ²¹	28 days
TOC	500 ml	P (disposable)	H ₃ PO ₄ to pH<2 Cool ≤6°C ²¹	28 days
DOC	500 ml <i>Include a Field Blank with DOC samples</i>	P (disposable)	Field filter using 0.45um pore size; H ₃ PO ₄ to pH<2 Cool ≤6°C ²¹	28 days

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Parameter ²	Minimum Required Volume	Container ^{1,14} P-Plastic G-Glass	Preservation ¹⁸	Maximum Holding Time ¹⁹
Turbidity	200 ml	P (disposable)	Cool $\leq 6^{\circ}\text{C}^{21}$	48 hours ⁶
Wet Chemistry Unit Parameters:				
Bromide Chloride Fluoride Sulfate	500 ml	P (disposable)	Cool $\leq 6^{\circ}\text{C}^{21}$	28 Days
Color: Platinum Cobalt	400 ml	P (disposable)	Cool $\leq 6^{\circ}\text{C}^{21}$	48 hours ⁶
COD	200 ml	P (disposable)	25% H_2SO_4 to $\text{pH}<2$ Cool $\leq 6^{\circ}\text{C}^{21}$	28 days
Cyanide, Total ²³	2 liters (2 x 1-liter bottles)	P	6N NaOH to $\text{pH} >10$, not exceeding a pH of 11; Cool $\leq 6^{\circ}\text{C}^{24}$ <i>Add 0.6 g ascorbic per bottle if chlorine present (see footnote 4)</i>	14 days <i>(24 hours if chlorine present and treated with ascorbic acid)</i>
Hexavalent Chromium	400 ml <i>Recommend field blank if sample(s) filtered</i>	P (disposable)	If sample is turbid, field filter using 0.45- μm pore size - followed by: Adjust pH to 9.3 – 9.7 using sample adjustment buffer ²⁵ Cool $\leq 6^{\circ}\text{C}^{21}$	28 days
MBAS	500 ml	P (disposable)	Cool $\leq 6^{\circ}\text{C}^{21}$	48 hours ⁶ <i>(notify lab)</i>
Oil & Grease	2 liters (2 x 1 liter-bottles)	G (wide-mouth quart jar, Teflon-lined cap)	1:1 H_2SO_4 to $\text{pH}<2$ Cool $\leq 6^{\circ}\text{C}^{21}$	28 days
Phenols, Total Recoverable	2 liters (2 x 1-liter bottles)	G <i>(Phenol bottle only)⁵</i>	1:1 H_2SO_4 to $\text{pH}<2$ Cool $\leq 6^{\circ}\text{C}^{21}$ <i>(1 ml Ferrous Ammonium Sulfate if sample contains oxidizer-prior to acid)</i>	28 days

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Parameter ²	Minimum Required Volume	Container ^{1,14} P-Plastic G-Glass	Preservation ¹⁸	Maximum Holding Time ¹⁹
Residue, Non-Filterable <i>-Total Suspended Solids</i> (plus Volatile/Fixed, if requested)	500 ml ²²	P (disposable)	Cool $\leq 6^{\circ}\text{C}^{21}$	7 days
Residue, Total <i>-Total Solids</i> (plus Volatile/Fixed, if requested)	500 ml ²²	P (disposable)	Cool $\leq 6^{\circ}\text{C}^{21}$	7 days
Residue, Filterable <i>-Total Dissolved Solids</i>	500 ml ²²	P (disposable)	Cool $\leq 6^{\circ}\text{C}^{21}$	7 days
Silica	200 ml	P (disposable)	Cool $\leq 6^{\circ}\text{C}^{21}$	28 days
Sulfide	120 ml (40 ml x 3) ²⁰	G 40-ml VOA vial with Teflon-lined septum	Add 0.1 ml of 2N zinc acetate plus 6 N NaOH to pH>9. Cool $\leq 6^{\circ}\text{C}^{21}$ <i>Leave no headspace in bottle.</i>	7 days
Other Parameters				
Hardness, Total <i>-request by checking Hardness, Total as CaCO₃, on field sheet. -or check Ca and Mg (can be part of metals sample)</i> <i>Total Hardness=2.497[Ca mg/L] +4.118[Mg mg/L]</i>	500 ml	P (disposable)	1+1 HNO ₃ to pH<2	6 months
pH	Inappropriate for laboratory analysis. Immediate - field measurement			
Carbon Dioxide <i>(Non-carbonate Hardness = total hardness- total alkalinity.) Non-carbonate Hardness⁽³⁾</i>	Inappropriate for laboratory analysis. Immediate - field measurement Submit samples for total hardness (Ca+Mg) and alkalinity (as specified above)			

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Parameter ²	Minimum Required Volume	Container ^{1,14} P-Plastic G-Glass	Preservation ¹⁸	Maximum Holding Time ¹⁹
Nutrients Unit Parameters:				
Ammonia (NH ₃ -N)	500 ml <i>(1 bottle for all, except when chlorine present; then include additional bottle of de-chlorinated sample for NH₃-N)</i>	P (disposable)	25% H ₂ SO ₄ to pH<2 ⁹ Cool ≤6°C ²¹ 0.008% Na ₂ S ₂ O ₃ to de-chlorinate (See note 11)	28 days
Nitrate-Nitrite (NO ₃ +NO ₂ – N)				
Total Kjeldahl Nitrogen (TKN)				
Total Phosphorus (TP)				
Dissolved Nutrients (4 parameters above)	200 ml (1 bottle)	P (disposable)	Field filter using 0.45um pore size; and then follow preservation above.	28 days
Nitrite (NO ₂ - N)	200 ml	P (disposable)	Cool ≤6°C ²¹	48 hour <i>(notify lab)</i>
Nitrate (NO ₃ -N)	Calculated value using analytical results for NO ₃ +NO ₂ -N and NO ₂ -N; Must submit samples for NO ₃ +NO ₂ -N and NO ₂ -N.			
Orthophosphate (PO ₄ -P)	200 ml	P (disposable)	Filter immediately through 0.45-micron filter; Cool ≤6°C ²¹	48 hours ⁶ <i>(notify lab)</i>
Metals Unit Parameters:				
Metals: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr (Total), Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, Zn, and Hg ¹⁹ .	500ml (1 bottle)	P (disposable)	1+1 HNO ₃ to pH<2, at least 24 hours prior to analysis	6 months (28 days for Mercury)
Boron	500 ml	P (disposable)	1+1 HNO ₃ to pH<2	6 months
Mercury EPA 1631 E Hg (trace-level total Hg)	500 ml of sample; <i>A Field Blank must accompany each trace-level Hg sample</i>	G (borosilicate), Teflon-lined cap	None required for total and dissolved Mercury; Use clean sampling techniques as described in EPA Method 1669.	28 days until preservation with BrCl ²² if the sample is oxidized in the sample bottle. Preserved samples are stable for up to 90 days from collection.

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 NCDWR-Water Sciences Section-Chemistry Laboratory

Parameter ²	Minimum Required Volume	Container ^{1,14} P-Plastic G-Glass	Preservation ¹⁸	Maximum Holding Time ¹⁹
Organics Branch Parameters:				
Acid Herbicides	4 liters ¹⁰	G (amber), Teflon-lined cap	Cool $\leq 6^{\circ}\text{C}^{21}$ 0.008% $\text{Na}_2\text{S}_2\text{O}_3$ (0.1ml 10% $\text{Na}_2\text{S}_2\text{O}_3$ /125 ml) ¹¹	7 days until extraction ¹⁶ <i>40 days after extraction</i>
Pesticides -Organochlorine -Organonitrogen -Organophosphorus	4 liters ¹⁰	G (amber), Teflon-lined cap	Cool $\leq 6^{\circ}\text{C}^{21}$ 0.008% $\text{Na}_2\text{S}_2\text{O}_3$ (0.1ml 10% $\text{Na}_2\text{S}_2\text{O}_3$ /125 ml) ¹¹	7 days until extraction ¹⁶ <i>40 days after extraction</i>
Semi Volatile Organics (Base/Neutral & Acid Extractables)	4 liters ¹⁰	G (amber), Teflon-lined cap	Cool $\leq 6^{\circ}\text{C}^{21}$ 0.008% $\text{Na}_2\text{S}_2\text{O}_3$ (0.1ml 10% $\text{Na}_2\text{S}_2\text{O}_3$ /125 ml) ¹¹	7 days until extraction <i>40 days after extraction</i>
TPH Diesel Range (aqueous)	4 liters ¹⁰	G (amber), Teflon-lined cap	Cool $\leq 6^{\circ}\text{C}^{21}$	7 days until extraction <i>40 days after extraction</i>
Volatile Organics (VOA)	40 ml x 4 ²⁰ <i>A Trip Blank (3 vials) must accompany all VOA samples.</i>	G, VOA vials Teflon-lined septum	Cool $\leq 6^{\circ}\text{C}^{21}$ 0.6g ascorbic acid only if residual chlorine present, Sodium Bisulfate (NaHSO_4) ¹³ to pH 2 ^{15, 17} . <i>Leave no headspace in bottle.</i>	14 days (7 days for aromatics only when unpreserved)
1,4-Dioxane	40 ml x 4 ²⁰ <i>A Trip blank (3 vials) must accompany all samples for 1,4- Dioxane</i>	G VOA vials, Teflon-lined septum	Cool $\leq 6^{\circ}\text{C}^{21}$ 0.008% $\text{Na}_2\text{S}_2\text{O}_3$ ^{11,24} <i>Leave no headspace in bottle.</i>	7 days
TPH Gasoline Range (aqueous)	40 ml x 4 ²⁰ . <i>A Trip blank (3vials) must accompany all VOA samples</i>	G, VOA vials Teflon-lined septum	Cool $\leq 6^{\circ}\text{C}^{21}$ 0.6g ascorbic acid only if residual chlorine present, Sodium Bisulfate (NaHSO_4) ¹³ to pH<2 ^{15, 17} . <i>Leave no headspace in bottle.</i>	14 days

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Key to Footnotes:

- (1) P-Plastic, G-Glass, P (Disposable)-Plastic disposable bottle.
- (2) Parameters grouped together e.g. Nutrients, may be submitted in the same bottle.
- (3) When non-carbonate hardness is requested, samples for both metals (Ca+Mg) and alkalinity must be submitted.
- (4) Add 0.6 g of ascorbic acid per 1-liter bottle only if sample contains residual chlorine; must be checked and treated for chlorine prior to pH adjustment.
- (5) Use one liter round glass bottles labeled phenol.
- (6) 48 hours is the maximum holding time; however, samples should be submitted to lab as soon as possible.
- (7) Use the 250-ml, wide-mouth sterile plastic bottles for all samples. All bottles contain sodium thiosulfate and EDTA reagents. Do not rinse.
- (8) To be NPDES-compliant, samples for coliform must be delivered to the laboratory within 6 hours of sample collection in order to meet the regulatory 8-hour hold time.
- (9) Caution: Addition of excessive amounts of acid will interfere with the test procedures. Sulfuric acid (H₂SO₄) preservative should be added using a graduated dispensing device, or from an ampule or vial containing pre-measured volume. Although the requirement is for pH<2, the ideal range for Nutrients is a sample pH of 1.5-2.0. For most ground water samples, this pH can be achieved by adding either 2.0 ml of 1:3 (25%) H₂SO₄ solution or 1.0 ml of 1:1 (50%) H₂SO₄ solution to 500 ml of the water sample. Confirm pH using pH test strips.
- (10) In a glass container, submit a small quantity of the pure compound of any suspected material.
- (11) Should only be used in the presence of residual chlorine. Add sodium thiosulfate or ascorbic acid (as specified) to the container first; fill at least half way before adding acid (if used). If residual chlorine is detected in a water sample (generally effluent), then it is recommended that the 500ml water sample for Nutrients be de-chlorinated at the time of sample collection. The recommended de-chlorination reagent is sodium thiosulfate (dissolve 3.5 grams in deionized water, then dilute to 1 liter). One mL of this solution will remove 1mg/L of residual chlorine in a 500 mL sample (prior to acid preservation).
- (12) Footnote no longer used.
- (13) Used by the DWR Chemistry Lab only at this time.
- (14) The container types listed are those commonly used throughout the Division. Other container types may be acceptable. Please consult the laboratory about use of proper containers before deviating from those listed above.
- (15) Samples submitted for purgeable halocarbons only should not be acid-preserved.
- (16) 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.
- (17) Samples submitted for purgeable aromatics receiving no pH adjustment must be analyzed within 7 days of collection.
- (18) Sample preservation should be performed immediately upon collection. For composite sample, 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 6°C until compositing and sample splitting is completed.
- (19) 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 setup. 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.
- (20) Fill the bottle to overflowing and cap, leaving no air space.
- (21) Aqueous samples must be preserved ≤ 6° C, and should not be frozen unless data demonstrating that sample freezing does not adversely impact sample integrity is maintained on file and accepted a valid by the regulatory authority. Also, for purposes of NPDES monitoring, the specification “≤ °C” is used in place of the “4 °C” and “< 4 °C” sample temperature requirements listed in some methods. The preservation temperature does not apply to samples that are analyzed immediately (less than 15 minutes).
- (22) Larger sample volumes may need to be submitted to achieve lower PQLs.
- (23) The QAO has a licensed copy of ASTM D7365-09a, which details sampling, preservation and mitigating interferences in water samples for analysis of Cyanide. Consult the Laboratory Quality Assurance Officer for mitigation instructions if any of the following interferences are suspect: sulfide, sulfur, aldehydes, sulfite, thiosulfate, thiocyanate, particulate cyanide, carbonate, nitrate-nitrite.
- (24) Dioxane testing is performed as outlined in EPA Method 624.1. EPA Method 624.1 is an approved Clean Water Act method in 40 CFR Part 136, which is an approved reference source in the 2L Rules. Preservation requirements are derived from 40 CFR Part 136.
- (25) For pH adjustment of water samples for hexavalent chromium, use Sample Adjustment Buffer solution provided by laboratory. Add 1 mL of buffer per 100 mL of sample. Confirm pH with narrow-range pH strip or pH meter.

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