

Sampling Water for Cyanide (CN), All Forms

PART 1 - BASIC SAMPLING PROCEDURE

BEFORE YOU BEGIN

- (1) When possible, ALL pretreatment and preservation steps must be completed WITHIN 15 MINUTES OF SAMPLE COLLECTION.
- (2) Unless otherwise specified, fill bottles to the bottom of the neck of the bottle. DO NOT RINSE, UNDERFILL, OR OVERFILL.
- (3) Put on latex or nitrile gloves, and other appropriate PPE, during sampling.

SAMPLING STEPS

- (1) Collect the water sample in **Bottle A (250-mL Poly)**.
- (2) Test for RESIDUAL CHLORINE (RC).
 - Remove the chlorine test strip from sleeve, dip it into the sample for 20 seconds with a constant, gentle back and forth motion, remove & shake once to remove excess water, wait 20 seconds for the color to develop, and within the next 20 seconds, determine if the color is:

(a) Yellow to yellow green	NEGATIVE	(zero to trace level chlorine)
(b) Light to dark olive green	POSITIVE	(0.01 to 0.10 mg/L chlorine)
(c) Light to dark blue green	POSITIVE	(0.10 to 0.20 mg/L chlorine)
(d) Dark shade of blue	POSITIVE	(>0.20 mg/L chlorine)
 - If the test strip was NEGATIVE, no pretreatment for chlorine removal is needed.
- (3) Test for SULFIDE (S).
 - Dip the sulfide test strip into sample, remove & shake once, and observe for color change.
 - If the test strip did NOT turn black, the sample is NEGATIVE for sulfide, and no pretreatment for sulfide removal is needed.
 - If the color changed to BLACK, the sample is POSITIVE for sulfide and needs to be treated. DO NOT SUBMIT SAMPLE without using the "Sulfide Removal Kit". If a "Sulfide Removal Kit" is not available, notify Paragon that this kit is needed. If a "Sulfide Removal Kit" is available, proceed with this procedure.
- (4) Record actions and observations from Steps (2) & (3) on FORM-N0013B.
- (5) Based on the results of Steps (2) & (3), pretreat and/or preserve the sample as follows:

Chlorine (RC) Result	Sulfide (S) Result	Procedure
NEGATIVE	NEGATIVE	Collect sample in Bottle B (120-mL Amber Poly w/NaOH) . Proceed to PART 3; <u>Submit Bottle B for CN analysis.</u>
POSITIVE	NEGATIVE	Collect sample in Bottle C (250-mL Poly w/AA) , cap, & mix. Then, transfer contents into Bottle B (120-mL Amber Poly w/NaOH) , cap, & mix. Proceed with PART 3; <u>Submit Bottle B for CN analysis.</u>
POSITIVE	POSITIVE	Collect sample in Bottle C (250-mL Poly w/AA) , cap, & mix. Then, follow the procedure in PART 2 using the "Sulfide Removal Kit".
NEGATIVE	POSITIVE	Follow the procedure in PART 2 using the "Sulfide Removal Kit" and the sample in Bottle A (250-mL Poly) .

PART 2 - SULFIDE REMOVAL PROCEDURE

BEFORE YOU BEGIN

- (1) Only use this procedure when results are POSITIVE for sulfide (S).
- (2) The "Sulfide Removal Kit" consists of a 250-mL Poly bottle labeled "Bottle D", a sealed bag containing a 60-mL plastic syringe and a 0.45-µm syringe filter; a sealed bag containing two 5-µm syringe filters, and a zip-seal bag labeled "5-µm Filter with Particulate".

SULFIDE REMOVAL STEPS

- (1) Use the water sample in **Bottle A (250 mL Poly)** or **Bottle C (250 mL Poly w/AA)**, as directed by Step (5) of PART 1.
- (2) Shake the sample bottle and determine if the sample contains visible particulates. If NO, go to Step (3); If YES, continue below.
 - Using the syringe with NO filter attached, draw up 50 mL of the sample, attach one of the 5- μ m filters, and inject the filtered water into **Bottle D (250 mL Poly w/PbCO₃)**. Remove the filter, place it in the small zip pouch identified as **5- μ m Filter with Particulate**, label the pouch, and submit this filter for CN analysis.
 - Again, using the syringe with NO filter attached, draw up 50 to 60 mL of the sample, attach the second 5- μ m filter, and inject the filtered water into **Bottle D (250 mL Poly w/PbCO₃)**. Repeat this step until **Bottle D** has been filled at least $\frac{1}{2}$ to $\frac{3}{4}$ full. (remove filter, draw up water, attach filter, inject into bottle). Then, proceed with Step (4).
- (3) Transfer enough sample from Step (1) to fill **Bottle D (250 mL Poly w/PbCO₃)** at least $\frac{1}{2}$ to $\frac{3}{4}$ full.
- (4) Cap **Bottle D**, and gently mix about 30 seconds to mix the contents. Allow the contents to settle for 1 to 2 minutes.
- (5) Using the syringe with NO filter attached, draw up 50 to 60 mL of the sample from the top of **Bottle D**, attach the 0.45- μ m filter, and inject the filtered water into **Bottle B (120 mL Amber Poly w/NaOH)**. Repeat this step a second time until **Bottle B** has been filled (remove filter, draw up water, attach filter, inject into bottle). Proceed with PART 3; Submit **Bottle B** for CN analysis.

PART 3 – ALDEHYDE AND/OR NITRATE TREATMENT PROCEDURE

- (1) If the sample contains aldehydes, or is suspected of containing aldehydes (e.g. wastewater), add the contents of the EDA vial to the sample in **Bottle B** and submit for CN analysis. Otherwise, simply submit **Bottle B** without adding the contents of the EDA vial for CN analysis.
- (2) If the sample contains high concentrations of nitrate, or is suspected of containing high concentrations of nitrates, add the contents of the sulfamic acid vial to the sample in **Bottle B** and submit for CN analysis. Otherwise, simply submit **Bottle B** without adding the contents of the sulfamic acid vial for CN analysis. [NOTE: The sulfamic acid vial is supplied only upon request and when prearranged.]

PART 4 - FINAL STEPS

- (1) Record the sampling date, time, site, and name of sampler on the labels for **Bottle B** and the small zip pouch containing the 5- μ m filter (if applicable), and the Chain-of-Custody (CoC) Record (FORM-N0013A). In addition, be sure that actions and observations recorded on FORM-N0013B agree with information on the CoC Record.
- (2) Begin to chill sample containers on natural ice, and maintain between >0 °C to 6 °C until transferred to the laboratory.
- (3) PLEASE RETURN all kits and kit materials, used or unused, to Paragon.

ACKNOWLEDGEMENT

I hereby acknowledge that I ___ have or ___ have not (check one) collected all submitted samples for cyanide (CN) as summarized above. I understand that not collecting samples using the above procedure may jeopardize the validity of any results obtained.

(Signature)

(Date)

Submit this document with the completed Chain-of-Custody Record that accompanies samples.

Attachment 1

Reference Information for Sampling Water for Cyanide (CN), All Forms

Bottles & Supplies in "Basic CN Kit":

- (1) 250-mL Poly bottle, labeled "Bottle A"
- (2) 120-mL Amber Poly bottle containing NaOH, labeled "Bottle B"
- (3) Sealed bag containing one 250-mL Poly bottle containing ascorbic acid (AA), labeled "Bottle C"
- (4) 2-mL Glass vial containing EDA
- (5) Ultra Low Total Chlorine Test Strip, in small zip bag
- (6) Sulfide Test Strip (containing lead acetate), in small zip bag
- (7) Water Pretreatment and Preservation Record (FORM-N0013B)

Bottles & Supplies in "Sulfide Removal Kit":

- (1) 250-mL Poly bottle containing lead carbonate (PbCO_3), labeled "Bottle D"
- (2) Sealed bag containing:
 - (a) one 60-mL plastic syringe (VWR #89213-178 or equiv.), and
 - (b) one 0.45- μm syringe filter (VWR #66030-837 or equiv.)
- (3) Sealed bag containing two 5- μm syringe filters (VWR #66064-395 or equiv.)
- (4) Small zip-seal pouch, labeled "5- μm Filter with Particulate"

Preservatives and/or Preservation Solutions:

- (1) AA (Ascorbic Acid [Vitamin C]), powdered, 50 mg per 250-mL bottle.
- (2) EDA (Ethylenediamine, 5.6% solution), 1.5 mL per 3-mL vial: Carefully dilute 1,414 μL of 99% EDA stock solution to 25 mL with PDI.
- (3) NaOH (Sodium hydroxide, 5N solution), 0.25 mL per 120 mL bottle: Carefully dissolve 200 g of NaOH pellets in 800 mL of PDI. Use CAUTION: The dissolving process is extremely exothermic. When cooled, bring the final volume to 1.00 L with PDI. Store in a labeled 1-L glass bottle. Transfer into the Dispensette bottle as needed.
- (4) PbCO_3 (Lead Carbonate), powdered, 250 mg per 250-mL bottle.
- (5) $\text{NH}_2\text{SO}_3\text{H}$ (Sulfamic acid, saturated solution), 1 mL per 3-mL vial: In a test tube, add ~1 g of sulfamic acid powder and ~5 mL of DI. Vortex, allow to settle, and use a transfer pipet to dispense 1 mL per vial (taking care to avoid the undissolved powder).

[NOTE: Sulfamic acid is not supplied in either kit. Prepare & supply only when requested.]

Notes:

- (1) Common KI-Starch test strips turn from white to blue to violet at approximately ≥ 1 mg/L chlorine.
- (2) Common lead acetate test strips turn from white to black at approximately ≥ 3 mg/L hydrogen sulfide.
- (3) The specified EDA addition is suitable to treat the interference from up to 50 mg/L CH_2O present.
- (4) USEPA, in method 524.2 stipulates 25 mg AA per 40 mL for each 5 mg/L chlorine, which is equivalent to 50 mg AA for 250 mL with 1.6 mg/L chlorine. According to the USDA, 1 g of ascorbic acid (AA) neutralizes 100 gallons of water with 1 mg/L chlorine (~2.64 mg/L AA treats 1 mg/L chlorine). This is equivalent to 0.66 mg AA for 250 mL with 1 mg/L, or 50 mg AA for 250 mL with 75 mg/L chlorine.