



Sampling, Preservation, and Mitigating Interferences in Cyanide Analysis Frequently Asked Questions

On March 12, 2007 (72 FR 11200) ⁽¹⁾, the U.S. Environmental Protection Agency (EPA) amended the analytical regulations of 40 CFR Part 136 for wastewater. A significant change was the addition of required cyanide preservation and sample pretreatment procedures to the footnotes of Table II, Required Containers, Preservation Techniques, and Holding Times. The preservation procedures included a consolidation of procedures that were present in existing EPA-approved cyanide methods and were based on knowledge available at the time. The EPA has received many comments concerning these cyanide footnotes. The commentary has centered on difficulties associated with collecting samples in the field, and cyanide formation as a result of high pH sample preservation procedures.

ASTM D7365-09⁽²⁾ is a result of extensive research on cyanide sampling, preservation, and mitigation of interferences. This ASTM practice attempts to provide solutions that make cyanide sampling easier and ensure results more closely represent the cyanide concentration present at the time of sampling.

It is the consensus of ASTM subcommittee D19.06 (committee on Methods for Analysis for Organic Substances in Water) that samples should be collected in amber glass bottles with minimal headspace, refrigerated to 4 – 6 °C, and analyzed within 14 days. ASTM also recommends ASTM methods D7237-06⁽³⁾, ASTM D6888-04⁽⁴⁾ (or OIA 1677⁽⁵⁾) with optional sulfide abatement; ASTM D7284-08⁽⁶⁾ and ASTM D7511-09⁽⁷⁾ be used if possible. These methods overcome many of the potentially undetected interferences likely to be present in environmental samples.

Commonly Asked Questions

1. What type of sample container and sample volume are recommended for collection of cyanide analysis samples?

Samples should be collected in amber glass, gas-tight vials to minimize exposure to ultraviolet radiation and narrow mouth bottles to minimize headspace. Collect a sample volume sufficient for the analytical method that will be used.

2. How should samples be preserved and what is the maximum holding time?

Unless otherwise specified, samples should be collected “as is” and analyzed within 14 days. Historically, sodium hydroxide (NaOH) has been added to preserve water samples for cyanide analysis; however, the addition of sodium hydroxide can cause a rapid decrease or increase in cyanide concentrations during storage.

3. How should samples be treated for sulfide interference?

If samples contain or are suspected of containing sulfide below the detection level of lead acetate test strips ($<50 \text{ mg/L S}^{2-}$), collect each sample “as is” and analyze using a method capable of analyzing cyanide in the presence of sulfide. ASTM D6888-04 (or OIA 1677) with optional on-line sulfide abatement reagent and ASTM D 7284-08/ASTM D7511-09 have been demonstrated to quantitatively recover cyanide in samples containing up to 50 mg/L S^{2-} .

If a sample contains enough sulfide to be detected using a lead acetate test strip ($>50 \text{ mg/L S}^{2-}$), dilute the sample with reagent water until sulfide is no longer detected (i.e., 10 mL sample diluted to 40 mL in a 40 mL VOA Vial). Indicate the dilution volume on the sample bottle and/or chain-of-custody form so dilution factors (total volume/sample volume) can be applied to calculate final results. Analyze the sample using a method capable of analyzing cyanide in the presence of sulfide. Colorimetric methods require samples containing sulfide be diluted below 10 mg/L S^{2-} .

4. How should I treat samples that may contain elemental sulfur? How can I tell if elemental sulfur is present?

If elemental sulfur is visibly present it will appear as yellow globules floating on the surface of the sample. These globules can simply be removed.

Colloidal (microscopic particles) elemental sulfur is not readily visible and reacts rapidly with cyanide lowering the result. There are no easy spot tests for colloidal sulfur. It is up to the permit holder to determine if colloidal sulfur is present or not. If colloidal elemental sulfur is believed to be present, samples must be filtered within 15 minutes of collection. If the sample is also known to

contain insoluble ferric ferro cyanide (Prussian blue), the solids should be retained for subsequent extraction and analysis. Otherwise, the particulates can be discarded.

5. How should I treat samples that contain oxidants (residual chlorine)?

Add reducing agent only if an oxidant is known to be present. Do not use ascorbic acid unless samples can be analyzed within 24 hours. Sodium arsenite (NaAsO_2) is preferred, however, if sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) is used, add only a sufficient quantity to destroy the oxidant. Do not add excess sodium thiosulfate.

6. How should samples that contain sulfite, thiosulfate, or thiocyanate be analyzed?

If samples contain sulfite, do not adjust the pH with sodium hydroxide. Sulfite, thiosulfate, and thiocyanate do not interfere with ASTM D6888-04 or U.S. EPA OIA 1677 available cyanide methods. However, they do interfere with all methods that utilize acid distillation and colorimetry. Because the Kelada-01 method is a distillation method it may not be satisfactory even though it is mentioned in the 72 FR 11200 Table II footnotes. ASTM developed D7284-08 and D7511-09 specifically to quantify total cyanide in the presence of sulfide, sulfite, thiosulfate, and thiocyanate.

7. How should samples containing particulate cyanide be handled?

Ferric ferrocyanide complexes (Prussian Blue) are very insoluble in acid solutions and require an extraction at high pH. If a sample contains particulates suspected of containing insoluble cyanide complexes the sample should be filtered and the solids reserved for alkaline extraction.

Older procedures involving distillation of the solids and liquid portion of a sample combined do not quantitatively recover cyanide present in a sample. Procedures that warm pH 12-13 samples at room temperature for 4 hours prior to distillation, risk the destruction or creation of cyanides.

8. How should samples with high carbonate content be handled?

High levels of carbonates can interfere with distillation methods by generating excessive foam that can distill into absorber solutions. High levels of carbonates (more than 1,500 mg/L) can interfere with amperometric methods generating negative bias. If samples are suspected of containing carbonates high enough to interfere, they should be treated with enough calcium hydroxide to precipitate the carbonate. Precipitate carbonate only if necessary. Alternatively, increase the molarity of the sodium hydroxide acceptor solution to up to 1 M if necessary.

References

1. Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; National Primary Drinking Water Regulations; and National Secondary Drinking Water Regulations; Analysis and Sampling Procedures. Fed. Regist. 2007, 47 (72), 11199–11249.
2. ASTM Standard D7365-09, “Standard Practice for Sampling Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide,” ASTM International, West Conshohocken, PA, www.astm.org
3. ASTM Standard D7237-06, “Standard Test Method for Aquatic Free Cyanide with Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection,” ASTM International, West Conshohocken, PA, www.astm.org
4. ASTM Standard D6888-04, “Standard Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection,” ASTM International, West Conshohocken, PA, www.astm.org
5. *Method OIA 1677, DW Available Cyanide by Flow Injection with Ligand Exchange*: 2004; EPA-821/R-04-001; U.S. Environmental Protection Agency, Office of Water, Engineering and Analysis Division
6. ASTM D7284-08, “Standard Test Method for Total Cyanide in Water by Micro Distillation followed by Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection”ASTM International, West Conshohocken, PA, www.astm.org
7. ASTM D7511-09, “Standard Test Method for Total Cyanide by Segmented Flow Injection Analysis, In-line Ultraviolet Digestion/Amperometric Detection”ASTM International, West Conshohocken, PA, www.astm.org



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