

New Findings on the Sampling and Preservation of Cyanide and Their Analytical Implications

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Cyanide Sampling and Preservation

- Scheme based on new rules in the footnotes of the Method Update Rule released March 12, 2007.
- Refer to *ASTM D7356-07 Standard Practice for Sampling, Preservation, and Mitigating Interferences in Water Samples for Analysis of Cyanide* for up to date procedures.

Sampling for Cyanide (Part 136)

- Step A:
 - **Collect** enough **sample** for the required analysis in clean amber glass containers.
- Decision point.
 - Is sulfide present?
 - Measured with lead acetate test paper.
 - Detects at ~ 50 ppm (brown color).
 - High iron – yellow color.

Sampling for Cyanide - No Sulfide Present


- No sulfide detected by lead acetate test strips (<50 ppm).
 - Can sample be analyzed within 48 hours?
 - Adjust the pH to 12 with NaOH and analyze within 48 hours.
 - Perform matrix specific holding time study to verify samples can be held longer than 48 hours without further treatment. (not specified by EPA)
 - Sample cannot be analyzed within 48 hours.
 - Proceed to Step B

Sampling for Cyanide – Sulfide Present

- Sulfide – positive to lead acetate paper (>50 ppm).
 - Analyte is total or available cyanide?
 - Proceed to step B.
 - Analyte is aquatic free cyanide.

Sampling for Cyanide – Sulfide Present

- Sulfide > 50 ppm – [analysis for aquatic free cyanide only.](#)
 - Adjust pH to 11 with NaOH.
 - Add 1 mg of powdered cadmium chloride per milliliter of sample.
 - Cap and shake container to mix.
 - After precipitate settles recheck with lead acetate paper.
 - Treat again if necessary.
 - Filter, refrigerate, and ship to laboratory.



Free Cyanide - ASTM D7237

- Free cyanide is defined as the amount of HCN liberated from a buffer solution adjusted to the pH of the receiving stream.
- The ASTM validation of free cyanide determined CN in a pH 6 solution.
- Free cyanide is the regulated species in SDWA, and the more reliable index of toxicity to aquatic life.
- Not a 40 CFR Parameter.

Sampling for Cyanide – Step B

- Elemental Sulfur Mitigation
 - Does sample contain elemental sulfur?
 - No – proceed to Step C
 - Yes
 - Filter within 15 minutes of sampling.
 - Save filter along with filtrate.
 - Presence of sulfur and metallic sulfides will cause CN results to be low.

Interferences – Sulfur Compounds

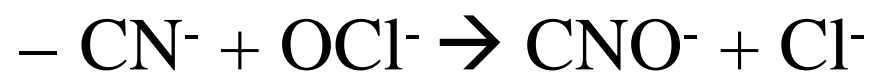
- Elemental Sulfur
 - $8\text{CN}^- + \text{S}_8 \rightarrow \text{SCN}^-$
- Metal Sulfides (distilling with solids present, or if sulfide complexing metals are added to distillation flask)
 - Cu_2S , FeS , PbS , CuFeS_2 , CdS , ZnS , etc.
 - S reacts with CN^- to form SCN^-

Sampling for Cyanide – Step C

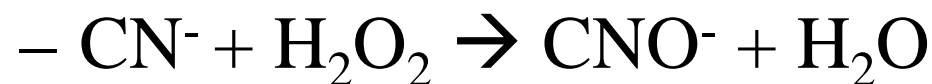
- Chlorine mitigation.
 - Does sample test positive to starch iodide paper? (Oxidizers present).
 - No.
 - Proceed to step D.
 - Yes.
 - Add ascorbic acid or sodium arsenite.
 - Proceed to step D.

Interferences – Oxidizers

- Hypochlorite



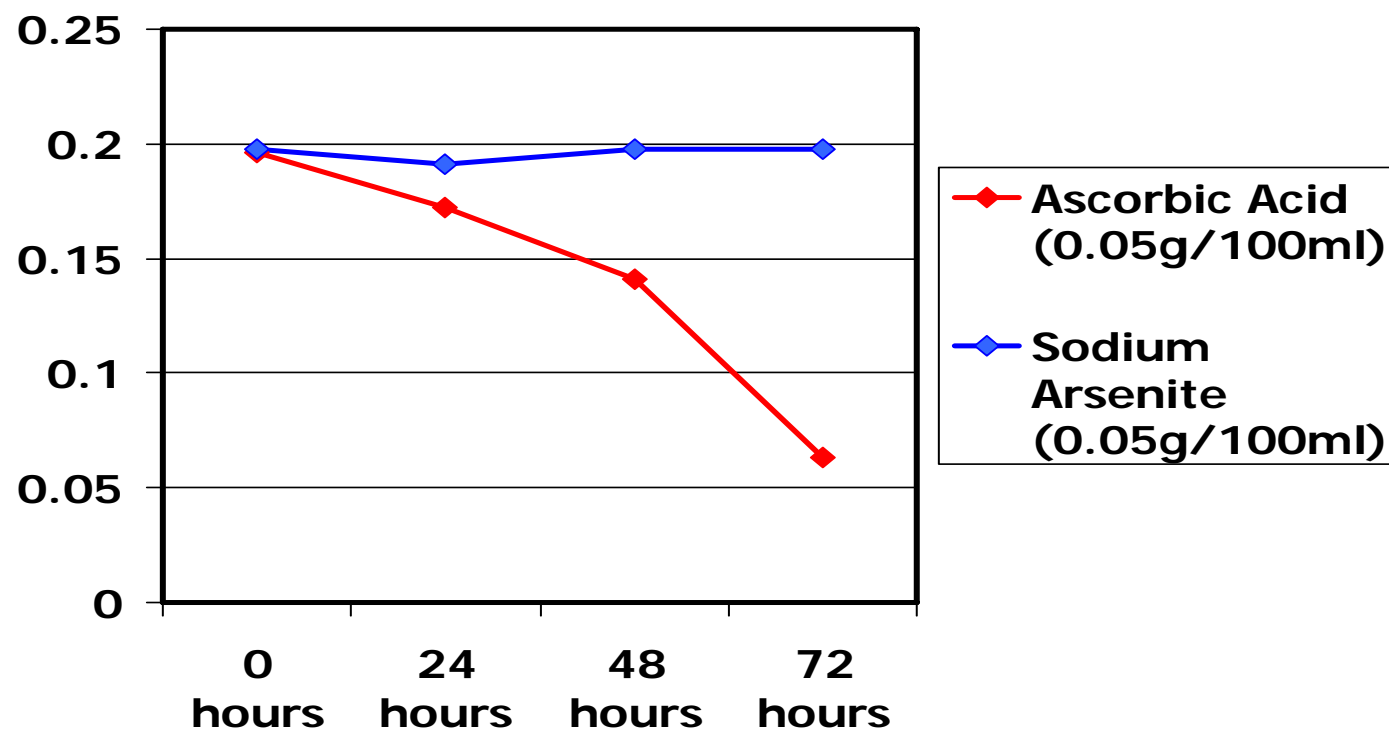
- Peroxide



- Caro's acid



Reducing Agents to Remove Oxidizers



0.2 mg/l CN as KCN added

Reducing Agents to Remove Oxidizers

- Sodium Sulfite and Sodium Thiosulfate both interfere with distillation procedures causing a **negative bias**.
 - Many papers report cyanide higher cyanide recovered when using ascorbic acid or sodium arsenite as a positive bias.
 - However, data presented later will demonstrate that sulfite and thiosulfate produce a negative bias with distillation.

Interferences - Oxidizers

- Chloramines can react with thiocyanate at pH 12 to create cyanide as samples are stored.



- Verify that holding time can be extended to 14 days, otherwise analyze dechlorinated and NaOH preserved samples within 48 hours.

Side Step into UV disinfection

- Peroxides, created with UV irradiation, react with thiocyanate to create cyanide.
 - $\text{SCN}^- + 3\text{H}_2\text{O}_2 \Rightarrow \text{HCN} + \text{SO}_4^{-2} + \text{H}^+ + \text{H}_2\text{O}$.
- Use of UV irradiation may cause effluents to be higher than influents.
- This is happening before samples are even collected. If UV disinfection is used it may be better to collect samples before and after.

Sampling for Cyanide – Step D

- Carbonate Mitigation.
 - Is sample high in carbonate, or high in alkalinity?
 - No.
 - Proceed to Step E.
 - Yes.
 - Use $\text{Ca}(\text{OH})_2$ instead of NaOH to adjust the pH of the sample to pH 12.

Sampling for Cyanide – Step E

- Sulfide mitigation
 - Did sample test positive with lead acetate paper?
 - No
 - Proceed to step F
 - Yes
 - Treat sulfide with one of the following:
 - » Volatilization
 - » Dynamic stripping
 - » Precipitation

Rationale – Sulfide Treatment

- Tests were made using an ASTM draft total cyanide method based on distillation followed by GD-amperometry.
- Available cyanide was determined by ASTM D6888-04.
- Special thanks to ASTM D19.06!

Precipitation Treatments for Sulfide

200 ppm S added

Addition of powder followed by filtration in < 2 minutes.
200 ppb CN as KCN added.

| Chemical Treatment | Avail. CN ug/L D6888-04 | % Rec |
|---------------------------|------------------------------------|--------------|
| Cadmium Carbonate | >2000 | > 1000 |
| Bismuth Nitrate | >2000 | >1000 |
| Lead Acetate | 149 | 74.5 |
| Lead Carbonate | >2000 | >1000 |

Precipitation Treatments for Sulfide

200 ppm S added

Addition of powder followed by centrifugation and filtration in < 15 minutes. 200 ppb CN as KCN added.

| Chemical Treatment | Avail. CN ug/L D6888-04 | % Rec |
|---------------------------|------------------------------------|--------------|
| Cadmium Carbonate | 193 | 96.5 |
| Cadmium Chloride | 181 | 90.5 |
| Lead Acetate | 66.9 | 33.5 |
| Lead Carbonate | 153 | 76.5 |

Precipitation of Sulfide With Cadmium

200 ppm S added

| CN Species | Avail CN ug/l | % Rec | Tot CN ug/l | % Rec |
|------------|---------------|-------------|-------------|-------------|
| KCN | 197 | 98.5 | NA | NA |
| Ferric CN | NA | NA | 2.66 | 1.33 |
| Mercury | 44.6 | 22.3 | 45.5 | 22.8 |
| Nickel | 176 | 88 | 165 | 82.5 |

Addition of Bismuth (Method 9010)

200 ppm S added

| CN Species | Total CN ug/l | % Rec |
|--------------|---------------|-------|
| KCN | 327 | 164* |
| Ferric CN | 267 | 134* |
| Sulfide only | 209 | NA |

Bismuth added to distillation flask according to method.

Detectable Sulfide in Absorber after treatment and distillation.

*** Corrected recoveries**

Addition of Bismuth to Samples

200 ppm S added

| CN Species | Total CN ug/l | % Rec |
|--------------|---------------|-------|
| KCN | 199 | 99.5 |
| Ferric CN | 101 | 50.5 |
| Sulfide only | 26.6 | NA |

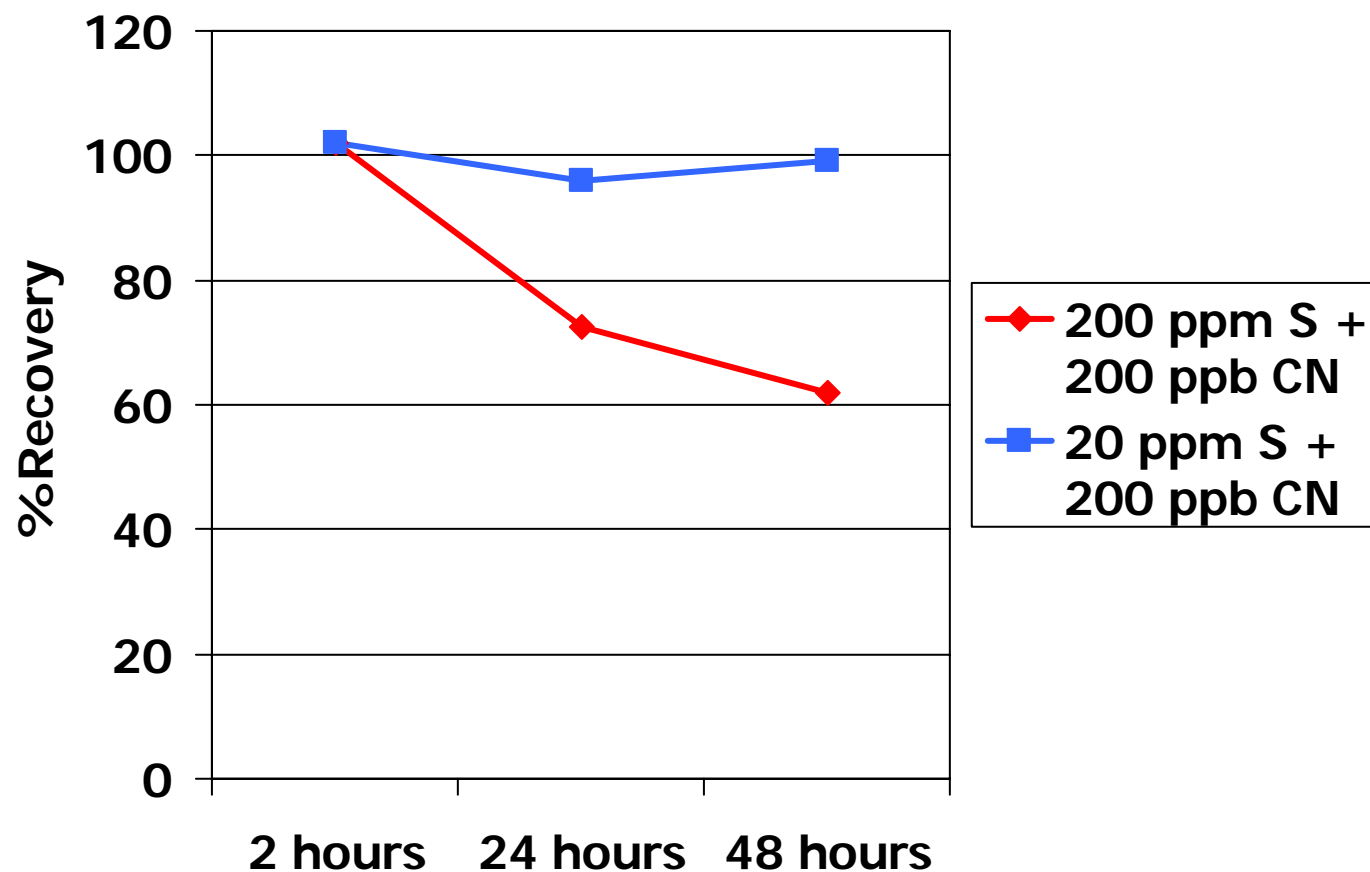
Sulfide precipitated from sample then filtered prior to distillation.

Sulfide Removal – Headspace or Dynamic Stripping

| CN Species | Avail. CN ug/l | % Rec |
|-------------------|---------------------------|--------------|
| KCN | 144 | 71.8 |
| Nickel CN | 168 | 83.8 |
| Mercury CN | 142 | 70.8 |

Detectable Sulfide was still present after treatment. Recoveries seem acceptable but detectable sulfide will lower cyanide over time.

Holding Time Study – Sulfide bearing samples.





Summary of Sulfide Treatments


- Precipitation – low recoveries.
- Headspace/Dynamic stripping – low recoveries and sulfide still present.
- **Dilution is the Solution** – the only real way to guarantee no interferences from sulfide is to dilute it out and run sample within 48 hours using a method that compensates for residual sulfide (proposed ASTM method based on ASTM D6888-04).

Sampling for Cyanide – Step F

- Aldehyde mitigation
 - Are aldehydes present? (Is sample disinfected by UV irradiation or ozone?)
 - No
 - Proceed to step G
 - Yes
 - Add 20 milliliters of 3.5% Ethylenediamine solution per liter of sample
 - Proceed to step G

Sampling for Cyanide – Step G

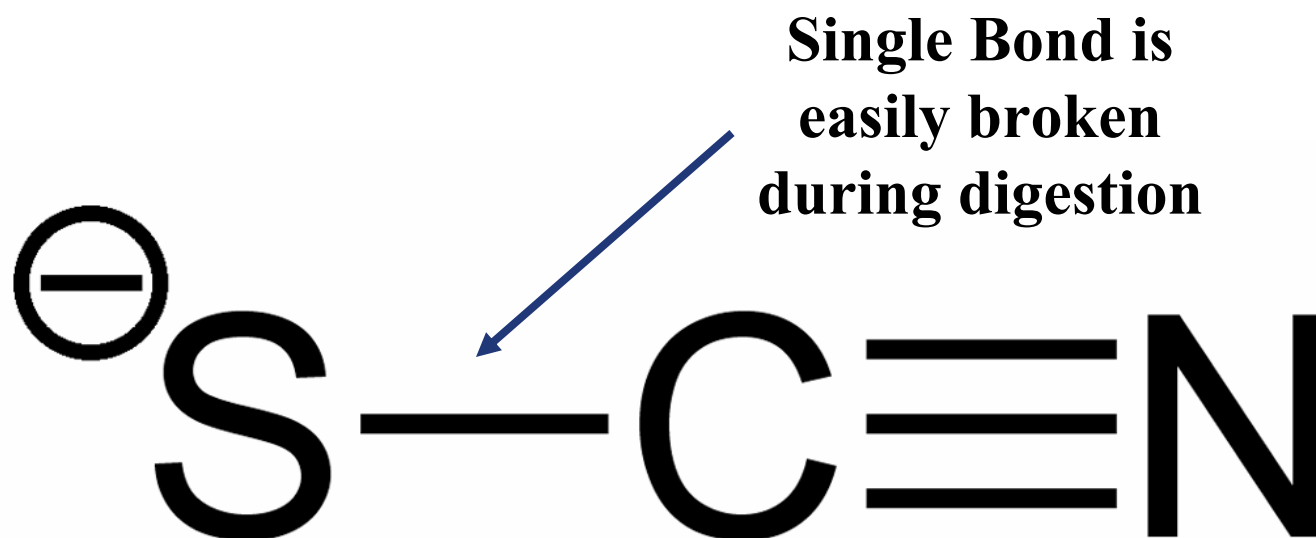
- Are sulfite, thiosulfate, or thiocyanate believed to be present?
 - No.
 - Preserve sample to pH 12 with NaOH, cool to < 6 C, and ship to laboratory.
 - 14 day holding time.
 - Yes.
 - Distillation will cause significant bias either positive or negative.
 - Use ASTM D6888-04.




Interferences – Thiocyanate

- Thiocyanate is present in almost all wastewaters (0.1–50 mg/l normal).
- The amount of thiocyanate present is enough to interfere with the distillation (the LACHAT Microdist method recommends not distilling if thiocyanate exceeds 0.2 mg/l).
- Interferences can be both positive (CN created) or negative (CN destroyed).
- There are no “spot” tests to determine thiocyanate.

Interferences – Thiocyanate





Interferences – Thiocyanate

- Thiocyanic acid, or HSCN, does not distill; however, the distillation process in the absence of oxidizers can form elemental sulfur, sulfur (IV) oxide, and carbonyl sulfide, which are converted to sulfide in the absorber solution.
- Sulfide in the absorber solution reacts with any cyanide to form thiocyanate and a negative bias.

Interferences – Thiocyanate

- 0.200 mg/L CN^- + 20 mg/L SCN^- :
 - Cyanide Found = 0.174 mg/L
 - Recovery = 87%
- 0.200 mg/L CN^- + 200 mg/L SCN^- :
 - Cyanide Found = 0.054 mg/L
 - Recovery = 27%

Interferences – Thiocyanate

- In the presence of Nitrate, thiocyanate decomposes to form CN^- , resulting in a positive bias (actual interference is from Nitrite).
- The addition of Sulfamic acid does not sufficiently reduce this interference.
 - A real POTW sample with 0.1 mg/L SCN^- and 63.5 mg/L NO_3^- **detected total CN^- at 0.10 mg/L** even after the addition of Sulfamic Acid.(1)

Interferences – Thiocyanate

| SCN ⁻ (mg/L) | NO ₃ ⁻ (mg/L) | CN ⁻ (mg/L) |
|-------------------------|-------------------------------------|------------------------|
| 0.100 | 1.00 | Not Detected |
| 0.100 | 10.0 | 0.010 |
| 0.100 | 25.0 | 0.017 |
| 0.100 | 50.0 | 0.060 |
| 0.100 | 100 | 0.086 |
| 1.00 | 10.0 | 0.009 |
| 1.00 | 50.0 | 0.038 |

False Positives

Interferences - Thiocyanate

- In another test:
 - 3 mg/l SCN + 5 mg/l NO₃-N distilled using the LACHAT microdist with CN analysis by GD-amperometry **resulted in CN = 10.9 ug/l.**
 - 15 mg/l SCN + 25 mg/l NO₃-N distilled using the LACHAT microdist with CN analysis by GD-amperometry **resulted in CN = 57 ug/l.**

Interferences – Sulfur Compounds

- Thiosulfate (used to dechlorinate)
 - 0.200 mg/L CN^- + 20 mg/L $\text{S}_2\text{O}_3^{-2}$
 - Cyanide Found = 0.124 mg/L
 - Recovery = 62%
 - 0.200 mg/L CN^- + 200 mg/L $\text{S}_2\text{O}_3^{-2}$
 - Cyanide Found = 0.040 mg/L
 - Recovery = 20%

False Negatives

Interferences – Sulfur Compounds

- Sulfite (used to dechlorinate)
 - 0.200 mg/L CN^- + 20 mg/L SO_3^{-2}
 - Cyanide Found = 0.080 mg/L
 - Recovery = 40%
 - 0.200 mg/L CN^- + 200 mg/L SO_3^{-2}
 - Cyanide Found = 0.000 mg/L
 - Recovery = 0%

False Negatives



Interferences – Sulfur Compounds

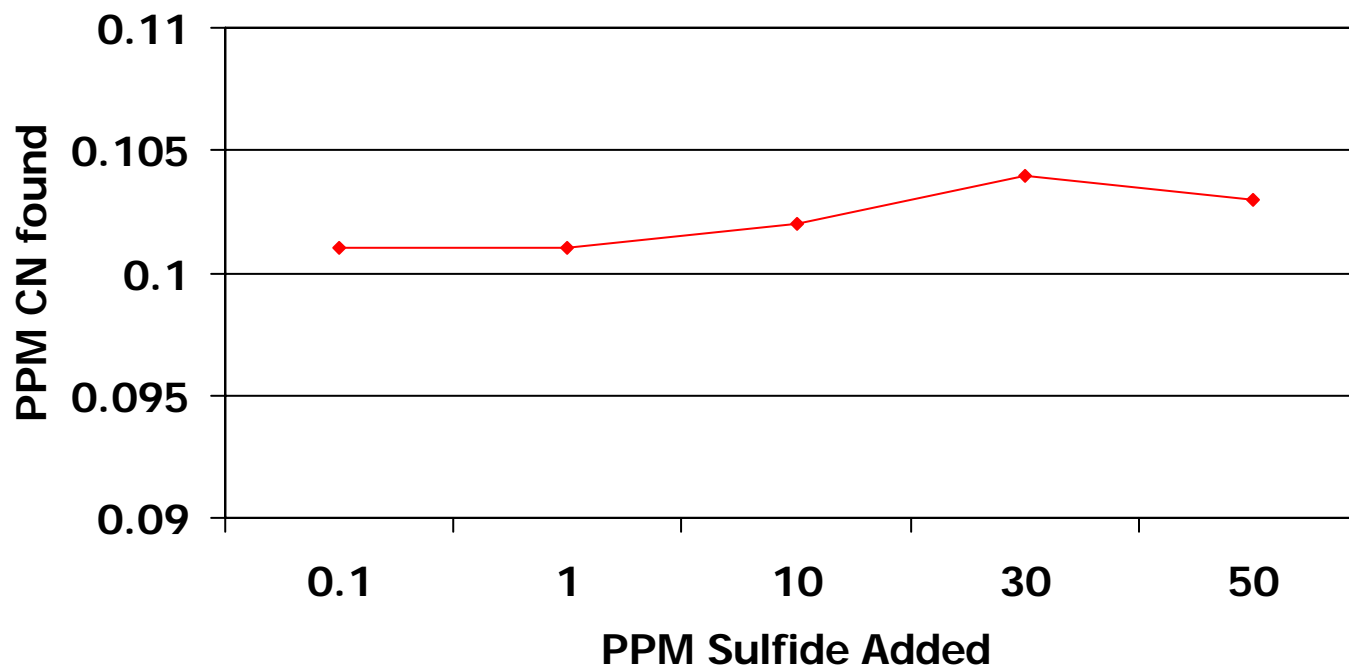
There are no “spot” tests that adequately detect the sulfur compounds that significantly interfere with total cyanide distillations.

Possible Interferences with GD-FIA methods – ASTM D6888-04/OIA 1677

| Ion | CN ⁻ Found (mg/L) Ratio Ion/CN ⁻ = 100 | CN ⁻ Found (mg/L) Ratio Ion/CN ⁻ = 1,000 |
|---|---|---|
| NH ₄ ⁺ | 0.200 | 0.202 |
| OCN ⁻ | 0.200 | 0.202 |
| SCN ⁻ | 0.200 | 0.204 |
| S ₂ O ₃ ⁻² | 0.205 | 0.204 |
| SO ₃ ⁻ | 0.199 | 0.201 |
| Br ⁻ | 0.197 | 0.202 |
| I ⁻ | 0.205 | 0.203 |
| CO ₃ ⁻² | 0.198 | 0.197 |
| NO ₂ ⁻² | 0.200 | 0.202 |
| NO ₃ ⁻² | 0.197 | 0.202 |

* All samples at 0.200 mg CN⁻/L

Method OIA 1677 or ASTM D6888-04 Sulfide Abatement



0.1 ppm CN added to varying amounts of Sulfide. **No Sulfide interference up to 50 ppm.**



“Total” Cyanide

- “Total” Cyanide is operationally defined as the amount of HCN liberated by distillation from a MgCl_2 /Sulfuric Acid Solution ($>100\text{ }^\circ\text{C}$, $\text{pH} < 1$).
- The HCN is absorbed into a sodium hydroxide solution and measured, usually Colorimetrically.
- By Definition, Total Cyanide does NOT include Thiocyanate or Cyanate

Interferences – Distillation

- The distillation step was designed to separate the cyanide ion from the previously listed interferences.
- In samples of well known and/or simple matrices, distillation is adequate.



Interferences – Distillation

- In complex samples, the combination of heat and high acid strength with other constituents in the sample can either destroy cyanide or create it.
- Automated on-line distillation (Kelada) methods for cyanide duplicate the conditions of manual distillations resulting in the same interferences.



Problems with Distillation Based Cyanide Methods

- Low repeatability and reproducibility (distillation precision and accuracy are operator-dependent).
- Multiple interferences.
- Time consuming and labor intensive sample preparation.

Accuracy/Precision Distillation Methods

| Laboratory | Sample 1 (mg/l CN) | Sample 2 (mg/l CN) |
|------------|-----------------------|-----------------------|
| A | 0.120 | 8.80 |
| B | 0.091 | 7.18 |
| C | 0.009 | 15.8 |
| D | < 0.002 | 11.5 |

Using EPA 335.2

Disadvantages with Distillation Methods

- Time Consuming
 - One hour long distillation (does not take into account setup and teardown)
 - CATC requires two distillations
- Bulky and Relatively Expensive Glassware
- Operator-dependent results (technique)
- Multiple Interferences



Proposed Total Cyanide Method

- ASTM draft method for total cyanide in water by manual distillation followed by gas diffusion – amperometric detection. (OIA 1677 or ASTM D6888).
- The method will be submitted for ballot in 2007, and is expected to be accepted for NPDES reporting once approved by the ASTM.
- This method eliminates the need for the pyridine-barbituric acid reagent.
- MDL = 0.003 mg/l on ferric cyanide complexes.
- The method produces accurate results in samples that are problematic with EPA 335.2 and 335.4.



Distillation Free Total Cyanide

- Draft method at ASTM.
- Based on OIA Method 1677 and ASTM D6888 Ligand Exchange Flow Injection-Gas Diffusion Amperometric methods for determination of Available Cyanide.

Distillation Free Total Cyanide

- Instead of ligands, metal cyanide complexes are “broken up” by UV irradiation.
- The method quantitatively determines the same cyanide species as “total” cyanide by distillation.
- Results are obtained in minutes instead of hours.



Why a Non-Distillation Method?

- Distillations are time-consuming.
- Distillation has a limited throughput.
- Distillation, though designed to separate cyanide from interferences, actually increases them.
- Cyanide measurements without distillation are more accurate.

Total Cyanide without Distillation

- Simplified method that does not suffer from the many interferences introduced by distillation.
- Cyanide complexes release cyanide after UV irradiation.
- The Hydrogen Cyanide formed diffuses into a dilute NaOH stream.
- Cyanide is determined amperometrically.

Total Cyanide without Distillation

| Species | Distillation Method 335.2 (% Recovery) | UV-Irradiation (% Recovery) |
|---------------------------------|---|--------------------------------|
| $[\text{Zn}(\text{CN})_4]^{2-}$ | 99.5 | 97.2 |
| $[\text{Cd}(\text{CN})_4]^{2-}$ | 104 | 104 |
| $[\text{Cu}(\text{CN})_4]^{3-}$ | 97.7 | 100 |
| $[\text{Ag}(\text{CN})_2]^-$ | 97.8 | 104 |
| $[\text{Ni}(\text{CN})_4]^{2-}$ | 104 | 98.3 |
| $[\text{Hg}(\text{CN})_4]^{2-}$ | 95.8 | 96.7 |
| $\text{Hg}(\text{CN})_2$ | 98.0 | 96.1 |
| $[\text{Fe}(\text{CN})_6]^{4-}$ | 101 | 102 |
| $[\text{Fe}(\text{CN})_6]^{3-}$ | 104 | 95.4 |
| $[\text{Pd}(\text{CN})_4]^{2-}$ | 69.1 | 17.7 |
| $[\text{Pt}(\text{CN})_4]^{2-}$ | 0.0 | 0.54 |
| $[\text{Pt}(\text{CN})_6]^{2-}$ | 0.0 | 0.0 |
| $[\text{Ru}(\text{CN})_6]^{4-}$ | 50.1 | 50.1 |
| $[\text{Au}(\text{CN})_2]^-$ | 56.6 | 49.5 |
| $[\text{Co}(\text{CN})_6]^{3-}$ | 0.0 | 13.8 |

Eliminating Interferences

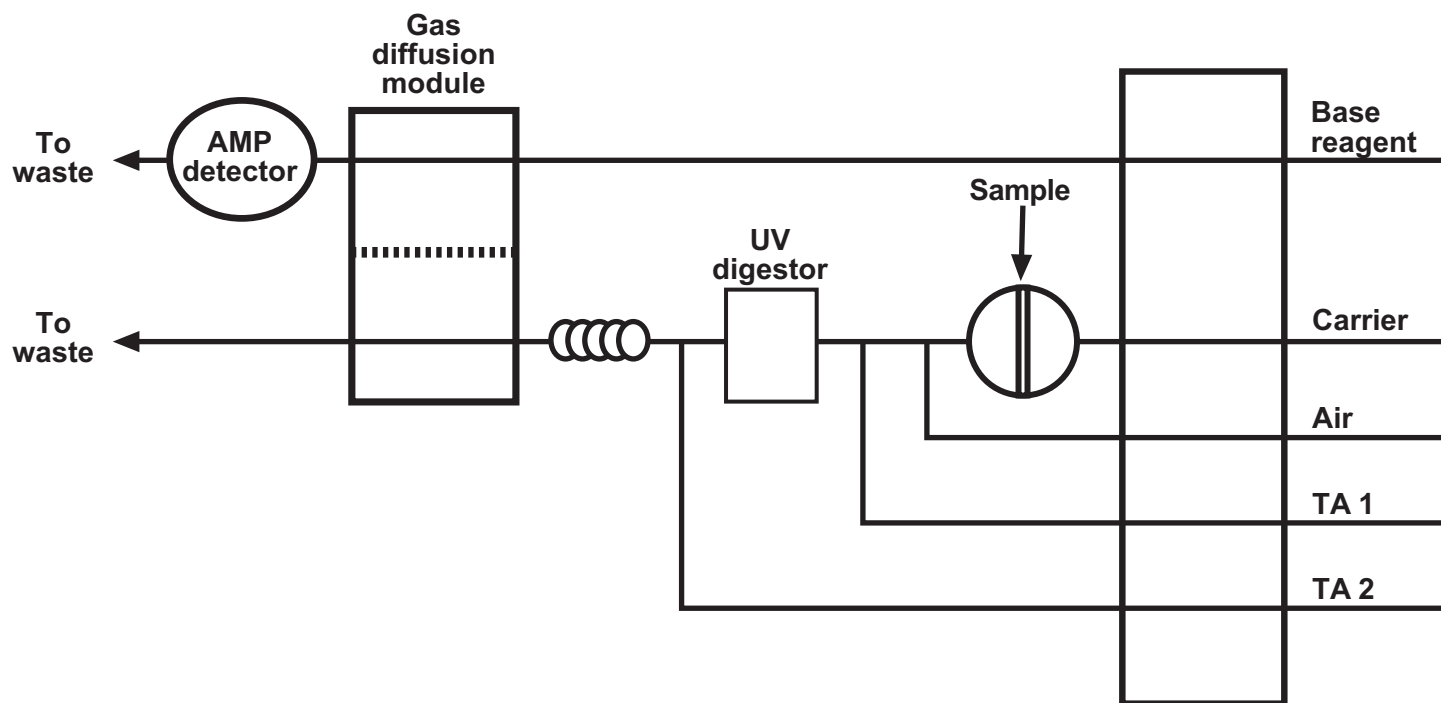
| Interfering Species Added at 20 mg/L | Untreated Samples Method 335.2 | Untreated Samples UV Irradiation | Treated Samples Method 335.2 | Treated Samples UV Irradiation |
|--------------------------------------|--------------------------------|----------------------------------|------------------------------|--------------------------------|
| Nitrite | 0.155 | 0.199 | 0.203 | 0.198 |
| Sulfite | 0.080 | 0.199 | No treatment | No treatment |
| Chlorine | Not Detected | Not Detected | 0.120 | 0.118 |
| Thiosulfate | 0.124 | 0.196 | No treatment | No treatment |
| Thiocyanate | 0.174 | 0.208 | No treatment | No treatment |
| Sulfide | Not tested | 0.198 | 0.120 | 0.189 |

* Cyanide added at 0.200 mg/L (EPA MCL SDWA)

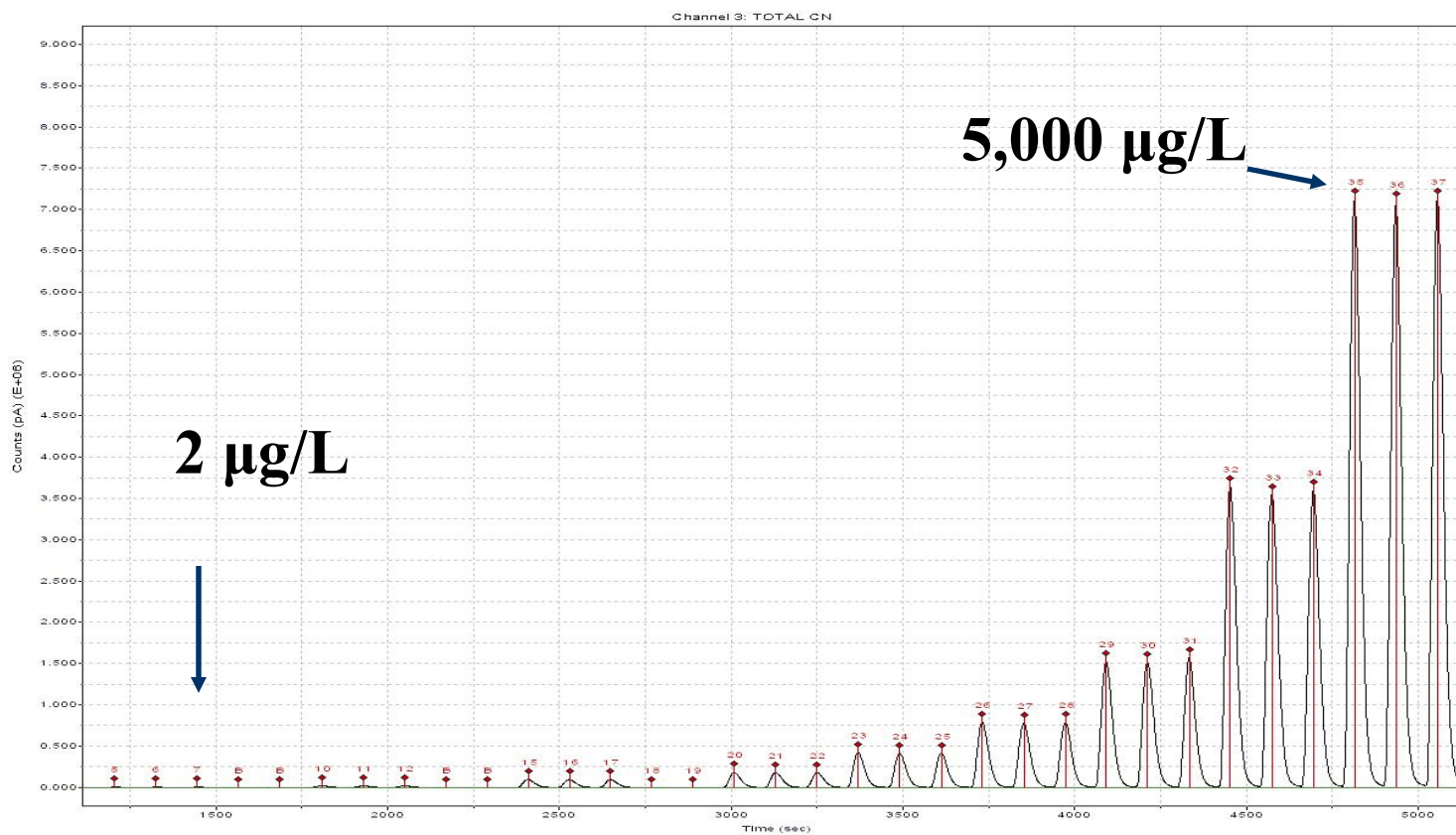
Total Cyanide without Distillation

- A simplified method that does not suffer from as many interferences as currently approved methods.
- Less than 1 mL of sample is required.
- Very little hazardous waste is generated.
- No pyridine-containing reagents.
- Amperometric detection is simple, very sensitive, selective, and has a large linear range.

Total Cyanide without Distillation



Total Cyanide without Distillation



Interferences – UV Irradiation Method

- Thiocyanate can photo decompose to form CN^- and S^{2-} , which are positive interferences.
- S^{2-} can be complexed after formation, eliminating its interference.
- Thiocyanate interference is minimized by UV irradiation >312 nm.
- High amounts of surfactants can “poison” the gas diffusion membrane.



References

- Zheng A., Dzombak D.A., Luthy R.G. *Effects of Thiocyanate on the Formation of Free Cyanide during Chlorination and Ultraviolet Disinfection of Publicly Owned Treatment Works Secondary Effluent*, Water Environment Research. Volume 76, Number 3, pp 205–212.
- Berman R., Christmann D., Renn C, *Automated determination of Weak Acid Dissociable and Total Cyanide without Thiocyanate Interference* American Environmental Laboratory, June 1993.



References

- WERF 2003, 98-HHE-5, Cyanide Formation and Fate in Complex Effluents and its Relation to Water Quality Criteria.
- OIA Draft Method 1678.
- OIA Method 1677.



Acknowledgements

- Connie Turner, South Carolina DHEC, Compiled Chart with Steps A – G.
- John Sebrosky Of Bayer Materials who collected numerous data points in his work as Task Chair for ASTM D19.06 Cyanide methods.