

# AVAILABLE CYANIDE SAMPLING AND ANALYSIS

by Mark Berthold, Lab Scientist

Michigan Department of Natural Resources and Environment



June 15, 2010

# CYANIDE FORMS

- Free/Reactive Cyanide
- Weak Acid Dissociable
  - Available
  - Amenable to chlorination
- Total Cyanide

# FREE / REACTIVE CYANIDE

- Hydrogen Cyanide (HCN) and Cyanide ION (CN<sup>-</sup>)
- Released at pH 6
- 1000 x more toxic to aquatic organisms than terrestrial organisms\*

# WEAK ACID DISSOCIABLE (AVAILABLE , AMENABLE)

- Free Cyanide
- Simple Cyanides
  - Sodium Cyanide (NaCN), Potassium Cyanide (KCN)
- Weak-Metal Compounds
  - Zinc, Cadmium
- Moderate-Metal Compounds
  - Copper, Silver, Nickel
- Released Under Mild Acid Conditions
  - pH 3-6

# TOTAL CYANIDE

- Free Cyanide
- Weak Acid Dissociable (WAD)
- Strong-Metal Cyanide Compounds
  - Iron, Cobalt, Gold
- Strong acid conditions (<math>< \text{pH } 2</math>), plus high heat and catalyst or UV dissociation for release

# TOTAL CYANIDE

All Forms Included



EPA 335.4, OIA1678/ASTM7511-09 etc.

# WEAK ACID DISSOCIABLE (AVAILABLE, AMENABLE)

**NO STRONG METAL CN**



# AVAILABLE vs. AMENABLE

- Both measure WAD cyanide
- Available measures directly with mild acid and ligand exchange chemistry
- Amenable uses total cyanide results before and after chlorination of the sample to calculate the result.



# Amenable Cyanide

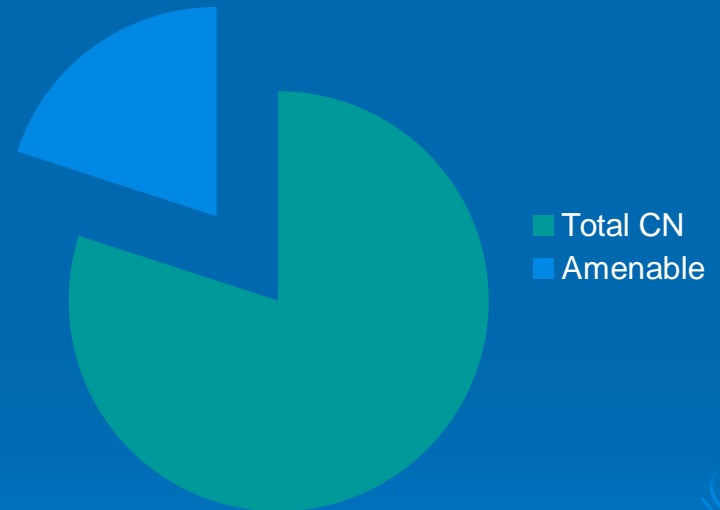
- Amenable to chlorination (CATC)
- Determine portion of cyanide (CN) in the sample that can be destroyed by chlorinating the sample.
- Sample is first run for Total CN.
  - ✓ If no Total CN detected, then no other forms of CN can be present.
  - ✓ If Total CN *is* detected, a second sample is chlorinated to destroy weak CN. Sample is then re-analyzed for Total CN.
- Difference between results is the “Amenable CN.”

# AMENABLE CN

Before Chlorination



After Chlorination



# AVAILABLE CN DIRECTLY MEASURED

## NO STRONG METAL CN



# SAMPLING ISSUES

## ➤ Interferences

- Sulfide
- Oxidizers (Chlorine)
- Carbonates
- Aldehydes

## ➤ Preservation

- Proper Sample pH
- Filtration

# SULFIDES

- Positive interference on available Cyanide test
- Degrades Cyanide in samples for all methods during storage
- Test sample with buffered lead acetate paper
  - Only shows positive for sulfide over 50 mg/l
  - *Available CN method (ASTM D-6888) eliminates sulfide interference up to 50 mg/l when using alternate acid reagent.*
  - ***Sulfide Reducing Acid Reagent***
    - *Bismuth Nitrate/Sulfuric acid.*
    - *Replaces HCl used in OIA-1677.*

# SULFIDES

- Samples positive for sulfide over 50 mg/l - treat with one of the following:
  - Dilute sample with deionized water until no longer positive, *record dilution*, preserve with NaOH and send to lab. Reporting limit will be raised by dilution factor.
  - Treat sample with lead carbonate, *filter immediately*, preserve with NaOH and send to lab

# SULFIDES

- Test sulfide removal technique by analyzing samples spiked with hydrogen sulfide.
- Verify CN recovery by spiking sample with both sulfide and cyanide and running test with interference mitigation.



# OXIDIZERS

- Test for Oxidizers with Buffered Potassium Iodide (KI) Test Paper
- Positive Results Require Treatment with Either of The Following
  - ASCORBIC ACID @ 0.6 g/L
  - SODIUM ARSENITE @ 0.1 g/L
- Preserve Sample and Send to Lab




# CARBONATES

- Negative Interference on Amperometric Tests
- Increasing Concentration of NaOH in Receptor Stream to 0.1 m Can Help Eliminate Interference
- Carbonate Levels Over 1500 ppm Can be Preserved with  $\text{Ca}(\text{OH})_2$  (Hydrated Lime) to Prevent Interference.

# ALDEHYDES

- Samples Known to Contain Water Soluble Aldehydes
  - Treat with Ethylenediamine Solution (EDTA)

# PARTICULATES

- Samples with high levels of particulate matter should be filtered prior to analysis.
  - Extract filter with NaOH and analyze filtrate.
  - Add results to value of sample.
- 

# PRESERVATION

- Preserve samples with NaOH
- pH should be as close to 12 as possible
- Check pH during addition of Sodium Hydroxide to avoid over preservation
- Holding time for properly preserved samples is 14 days

# SEDIMENT SAMPLES

- Extracted at laboratory – Method 9013
- Extract samples in rotator for 16 hours at pH 12 (NaOH)
- Interferences mitigated at lab prior to analysis.
- Same potential interferences for water samples apply.

# SUMMARY OF METHOD

- Sample is treated with ligand exchange reagent.
- Treated sample is acidified in a flow-injection analyzer to form hydrogen cyanide.
- HCN gas is diffused through a gas permeable membrane in to an alkaline (NaOH) acceptor stream and sent to amperometric detector.
- Electrical current measured at the detector is proportional to cyanide concentration in standard or sample.

# TROUBLESHOOTING

- Electrode maintenance.
  - Low voltage response – clean electrode.
  - Don not let electrode dry out between uses.
- Diffusion membrane
  - Low recovery – inspect, change membrane.
- pH issues
  - Sample must not be over- preserved.
  - Keep pH as close to 12 as possible
- Before each run inject 3 high standards into system.
  - Don't start run until RSD is  $< 5\%$


# NEW METHODS ON THE HORIZON

- Potential changes to EPA 40 CFR Part 136
- New methods likely to be approved
- ASTM D-7511-09(OIA1678)
  - Total Cyanide By in-line UV digestion, gas diffusion and amperometric detection
- ASTM D-7284-08
  - Total Cyanide by distillation (macro or micro) with gas diffusion and amperometric detection



# PRESERVATION GUIDELINES

## ASTM D-7365-09

- Likely to be approved as supplement to current preservation / interference mitigation protocols.
  - Generally recommends diluting interferences rather than adding chemicals and using amperometric detection for analysis.
  - Consider as alternative option to current techniques rather than mandate.
- 

# Cyanide Sampling and Analysis

Questions

