

# Cyanide Compliance

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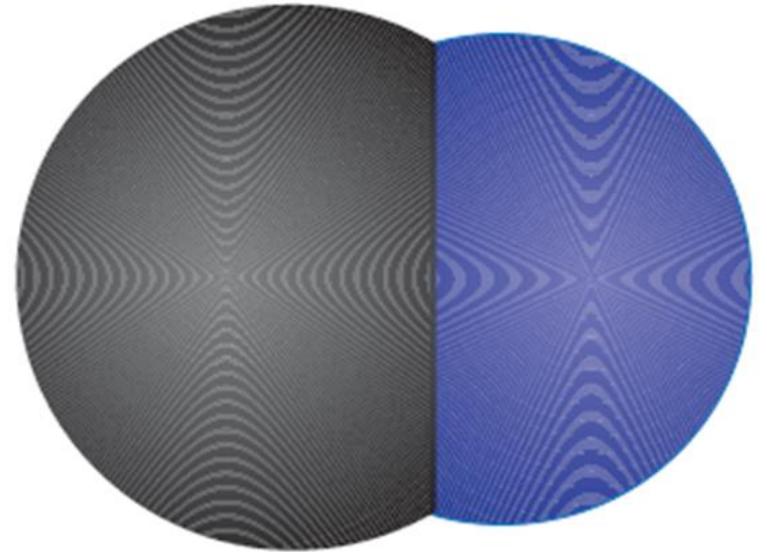


# Cyanide in WWTP Effluent

- Sample results showing the presence of cyanide may be “false” positives
- History of “random” cyanide in IV goes back at least 10 years
- EPA has been aware of analysis problems when analyzing for cyanide in “complex” effluents such as domestic wastewater
- R7 desires to know whether there is indeed a threat to water quality

# Objectives

- Sources of Cyanide
- Cyanide species
- Analysis interferences
- 2012 40 CFR 136
- Representative samples



# Sources of Cyanide

- Naturally occurring: lima beans, almonds; pits of apricot, apples, peaches
- Combustion products including cigarette smoke
- Cyanide salts in metallurgy for electroplating, cleaning and gold ore processing
- Cyanide gas used to eliminate pests and vermin in buildings and ships



# Cyanide Species

Cyanide (A); Cyanide and Thiocyanate –Total;  
Cyanide Complexed to Range of Compounds;  
Cyanide, Free Not Amenable to Chlorination; Cyanide  
in Bottom Deposits (dry weight); Cyanide Sludge  
Solid; Cyanide Filterable, Total; Cyanide, Free-Water  
plus Wastewaters; Cyanide Total (as CN); Cyanide,  
Total Recoverable; Cyanide, Weak Acid Dissociable;  
Cyanide, Dissolved (Std. Method); Cyanide, Free  
(Amenable to Chlorination); **Cyanide Free.**

Source: State Water Resources Control Board (SWRCB) Water Quality Enforcement Policy, May 20, 2010

# Cyanide Species cont.

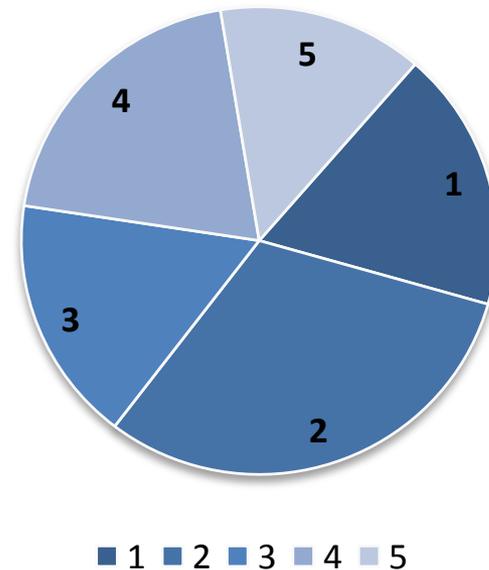
Schematic illustration of how different cyanide species are defined based upon the method of analysis used in the laboratory.

## Analysis Methods:

- Total Cyanide = (1+2+3+4+5)
- Transition Metal Cyanocomplexes = (1+2+3+4)
- Cyanide Amenable to Chlorination = (1+2+3)
- Weak Acid Dissociable Cyanide (1+2)
- Free Cyanide\*\* = (1)

\*\* Only species toxic to aquatic life

## Cyanide



# 40 C.F.R. 136

- Before 2012 U.S. EPA approved methods for:
  - Total cyanide:
    - EPA 335.2; 335.3; 335.4, and
    - SM 4500-CN C, D, E and F
  - Available cyanide (weak acid-dissociable):
    - SM 4500-CN G
- After 2012 U.S. EPA approved methods for:
  - Free cyanide



# Analysis and Interferences

- Total and Available Cyanide methods
  - Overestimate the toxicity of the effluent
- Interferences
  - Sample preservation in NaOH (high pH)
  - Nitrate, nitrite, sulfides in the wastewater
  - Chlorination and UV disinfection
  - Sample holding time
- Problem
  - False positives = added expenditures
  - Under-reporting = threats to WQ not identified

# New Methods for Free Cyanide\*\*

<b>ASTM Standard Practice D7237-10</b>	<b>Amperometric (Automatic – FIA):</b> Passive diffusion of cyanide at pH 6 to pH 8. <b>Approximate range: 2 to 500 µg/L</b>
<b>OIA-1677</b>	<b>Amperometric (Automatic – FIA):</b> Passive diffusion of cyanide at pH 6 to pH 8 <b>Approximate range: 2 to 5,000 µg/L</b>
<b>ASTM Standard Practice D4282-02</b>	<b>Calorimetric (Manual):</b> Passive diffusion of cyanide at pH 6 Sample is chlorinated + reagent for color <b>Approximate range: 10 to 150 µg/L</b>

\*\* CFR 40 Part 136 May 2012

Cyanide “hits” - Rats!

What do I do now?



# Cyanide “hits” - What to do?

- The goal is to collect data that is representative of effluent quality.
- Four areas of investigation (not necessarily in order)
  1. Source control
  2. Laboratory
  3. Sample collection/preservation
  4. Sampling for representative results
- Prepare documentation for reporting purposes



# Source Control

- Source control – verify that your community does not have a:
  - Gold mine and/or ore processing facility,
  - Artist's photography studio – sepia toning,
  - Metal/chrome plating facility w. discharge to sewer,
  - Pest exterminator using cyanide gas,
  - Laboratory using reagents containing cyanide, or
  - Facility producing nylon or plastics
- Review permits, CUPA\*\*, business licenses, etc.
- Document and report results

\*\*Certified Unified Program Agency (CUPA) for Hazardous Materials Management

# Laboratory

- Verify that laboratory is using the method of analysis *you* want\*\*
- Laboratory to do triplicate analysis (for free) to investigate laboratory variability
- Document and report results

\*\* e.g. Free Cyanide



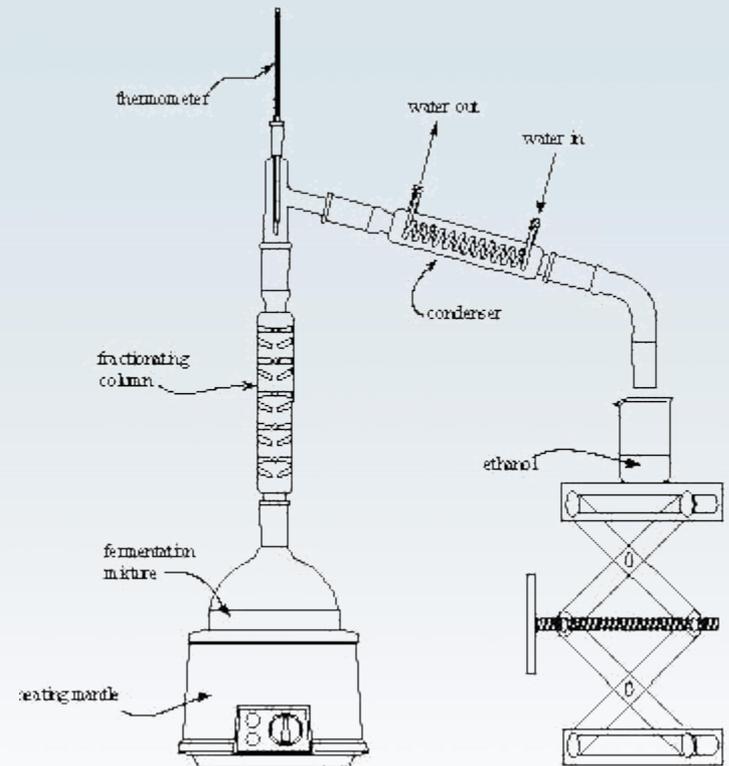
# Sample Collection/Preservation

- Collect sample before and after disinfection
- If there is reason to believe that effluent solids do not contain cyanide particulates (source control) filter sample
- Treat sample for potential nitrate and sulfide interference – work with lab to refine sample collection
- Preserve sample in NaOH pH>10 (not pH>12) – work with lab to prepare appropriate sample bottles
- cont.



# Sample Collection/Preservation (cont.)

- Laboratory to collaborate/assist with sampling study
  - Before/after disinfection
  - Holding times
  - Before/after preservation
- ASTM D7365-09a
  - Flexible approach for sample handling and managing interferences



# Sampling for Representative Results

- Sample early in sampling “period” to make sure you have time to verify results
- Collect multiple grab samples on the sample day
- Analyze sequentially



# Multiple daily grabs

- Procedure:
  - Collect sample and preserve as required
  - Analyze the first sample
    - Criteria: Chronic **5.2**  $\mu\text{g}$  CN/L (free cyanide).
    - If  $< 5.2$   $\mu\text{g}$  stop
    - Else, analyze 2<sup>nd</sup> sample,
    - Repeat
- Analyze results through a ranking process

# Multiple daily grabs (cont.)

- Analysis using a Ranking Process:
  - Rank sample results
  - Determine **median** value
  - Assess results = compliance/violation



# Multiple daily grabs (cont.)

- Example 1:
  - 1<sup>st</sup> sample = 4.2  $\mu\text{g}$
  - Stop
  - **Permittee is in compliance**



# Multiple daily grabs (cont.)

- Example 2:
  - 1<sup>st</sup> sample = 18  $\mu\text{g}$
  - 2<sup>nd</sup> sample = ND
  - Ranking: 18: ND
  - Result: ND
  - **Permittee is in compliance**



# Multiple daily grabs (cont.)

- Example 3:
  - 1<sup>st</sup> sample = 18  $\mu\text{g}$
  - 2<sup>nd</sup> sample = 5.0  $\mu\text{g}$
  - Ranking: 11.5  $\mu\text{g}$  > 5.2  $\mu\text{g}$
  - **Permittee is in Violation**
  - 3<sup>rd</sup> sample = ND
  - Ranking: 5.0  $\mu\text{g}$
  - **Permittee is in compliance**



ANY  
QUESTIONS  
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