Cyanide Compliance

Anders Wistrom RWQCB

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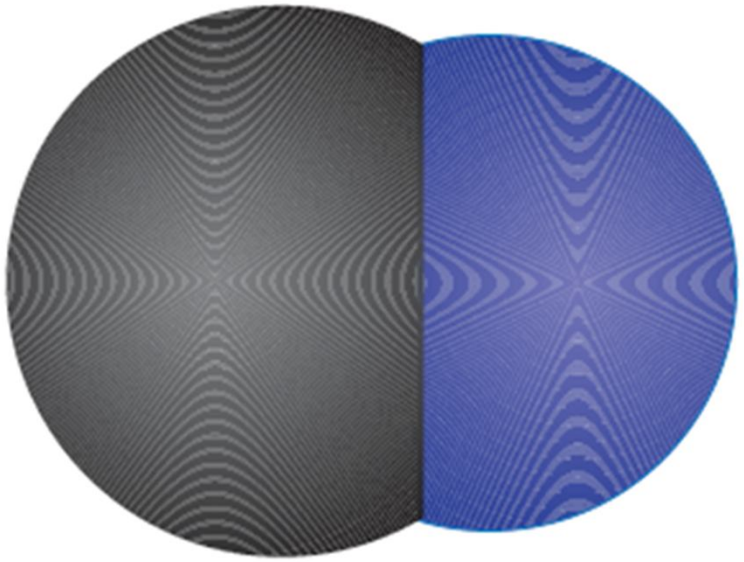
CALIFORNIA
Water Boards

Cyanide in WWTP Effluent

- Sample results showing the presence of cyanide may be “false” positives
- History of “random” cyanide in R7 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 and sampling strategies



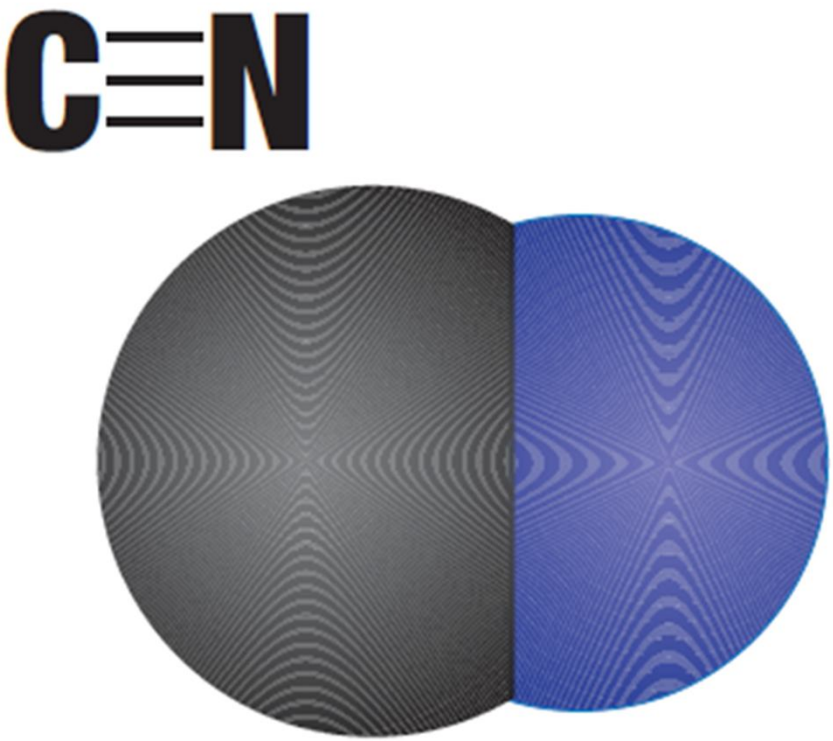
Sources of Cyanide

- Carbon + Nitrogen
- Triple bond
- You can make cyanide:

$$CH_4 + NH_3 \xrightarrow{T°+Pt} H - C \equiv N + 3H_2$$

T° High temperature

Pt Catalyst



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

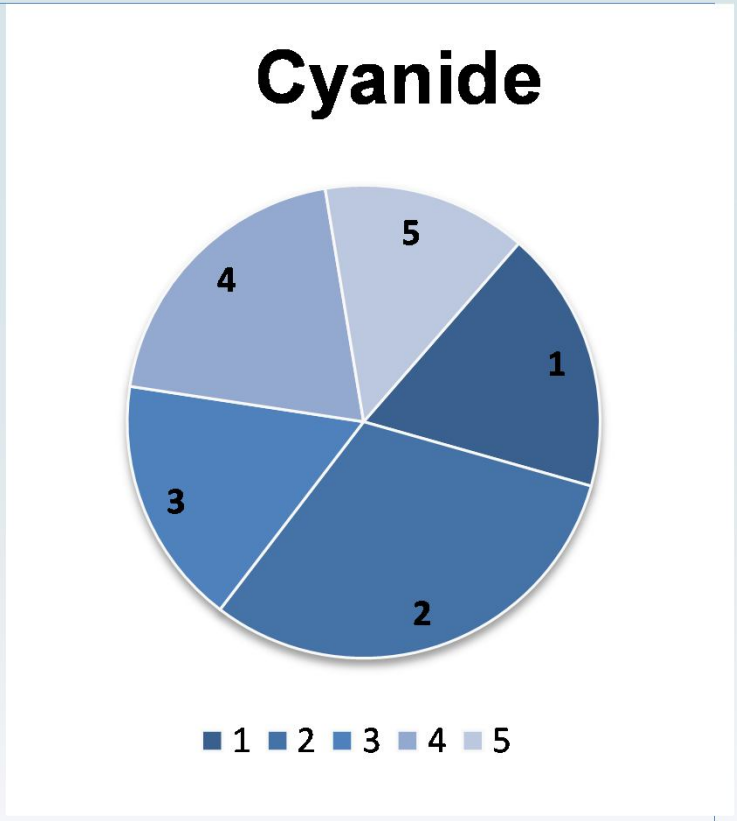
Cyanide Species

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.



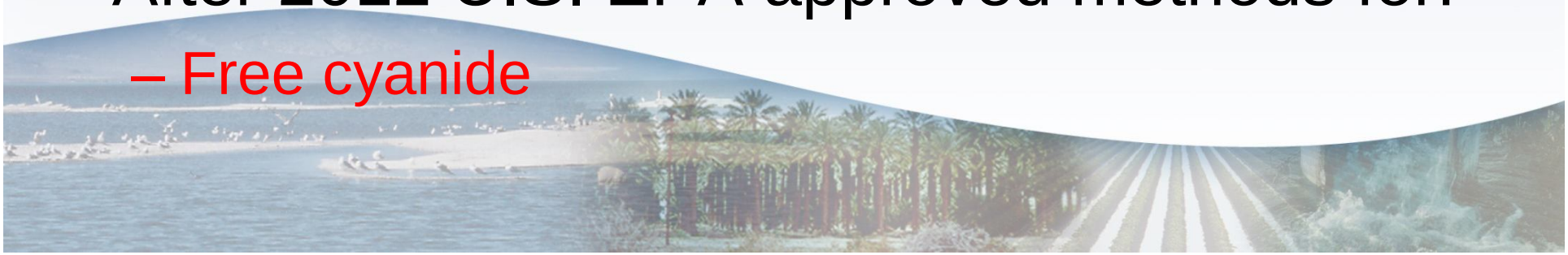
Analysis Methods:

- 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

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**

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

** 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

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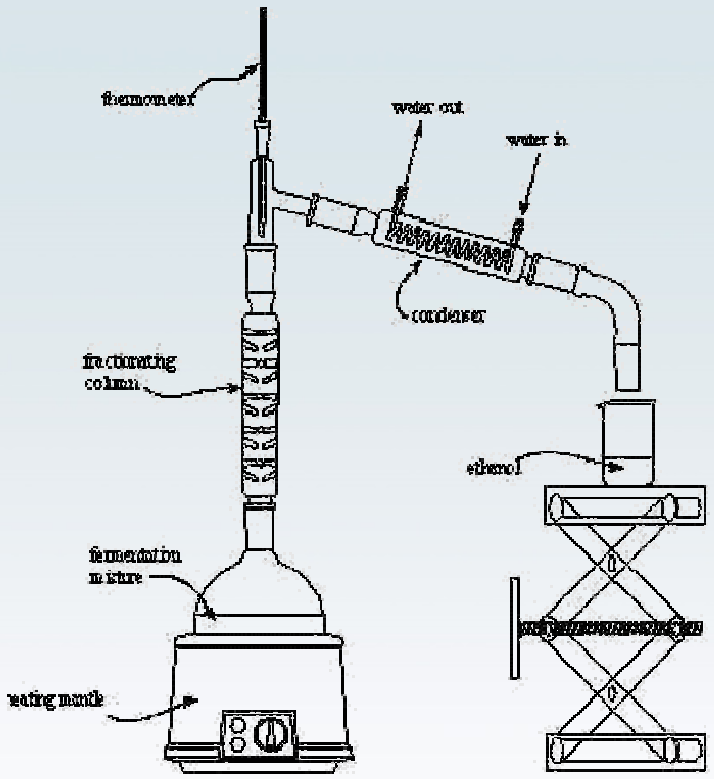
Sample Collection/Preservation

- 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** µg CN/L (free cyanide).
    - If < 5.2 µg stop
    - Else, analyze 2nd 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:
  - 1st sample = 4.2 µg
  - Stop
  - **Permittee is in compliance**

Multiple daily grabs (cont.)

- Example 2:
  - 1st sample = 18 µg
  - 2nd sample = ND
  - Ranking: 18: ND
  - Result: ND
  - **Permittee is in compliance**

Multiple daily grabs (cont.)

- Example 3:
  - 1st sample = 18 µg
  - 2nd sample = 5.0 µg
  - Ranking: 11.5 µg>5.2 µg
  - **Permittee is in Violation**
  - 3rd sample = ND
  - Ranking: 5.0 µg
  - **Permittee is in compliance**


ANY
QUESTIONS
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