Cyanide Interference in Effluent Samples and How to Avoid It

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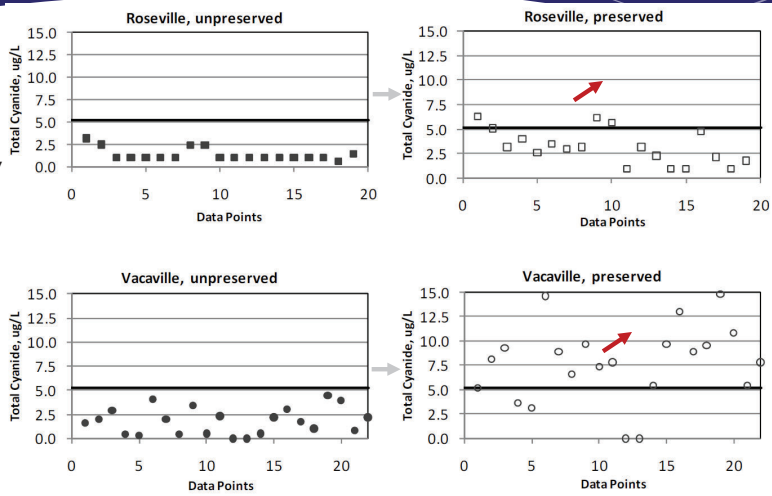
Problem Statement

- Total cyanide (CN) analyses of treated municipal wastewater effluent can be compromised by analytical interferences
- The required preservative (NaOH) can cause interference resulting in false positives (i.e., > WQC)
- Acid distillation methods have greatest potential for interferences – and are the most common analyses for total CN.

NaOH – Sodium Hydroxide
WQC – Water Quality Criterion



Total cyanide analyses in split samples, one preserved with sodium hydroxide and the other unpreserved (Giudice et al. 2010). Data from the City of Roseville Pleasant Grove and Dry Creek Wastewater Treatment Plants (hold-time was 1 to 2 hours) and the City of Vacaville Easterly Wastewater Treatment Plant (hold time was less than 15 minutes).

Presentation Overview

Sampling / Regulatory / Analytical Requirements

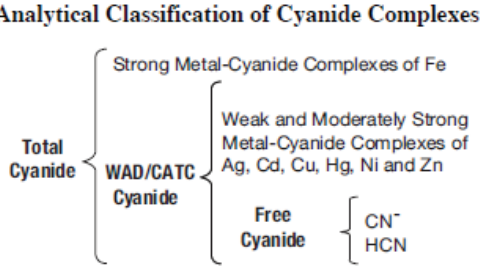
Study Approaches

Case Studies

Regulatory Requirements (WWTP Effluent)

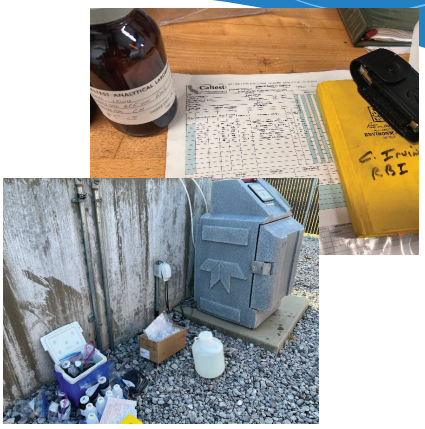
- California Toxics Rule (CTR)
  - Chronic Criterion: 5.2 µg/L (4-day average)
  - As free CN
- <u>Total</u> CN required by (most) NPDES permits
- <u>Target RL</u> of 5 µg/L
- Detections of total CN can trigger
  - Effluent limitations, routine monitoring
  - Compliance issues (violations/MMPs)
  - Trigger local limits for Pretreatment Programs

Analytical Classification of Cyanide Complexes



CATC – CN amenable to chlorination; ERWC – Effluent and Receiving Water Characterization; MMPs – Mandatory Minimum Penalties

Analytical Requirements - Sampling



- Samples must be collected as grabs
- Samples must be preserved if analyzed >15 minutes after collection
  - Sodium hydroxide (NaOH) preservative
    - pH ≥10*
    - Often provided by lab in excess
    - Hold time of 14 days
- No preservative if analyzed within 15 minutes

**Methods may indicate preservative to pH 12, but this is superseded by 40 CFR §136.3(e) – 2021 Method Update Rule indicating preservation to pH 10*

Study Approaches

- 40 CFR § 136.3(e) – Footnote 6 in Table II
  - Allows any technique to remove or suppress interference associated with sampling and preservation when doing so will provide more accurate cyanide measurements
  - No Alternative Testing Procedure (ATP) required

Designation: D7365 – 09a (Reapproved 2015)

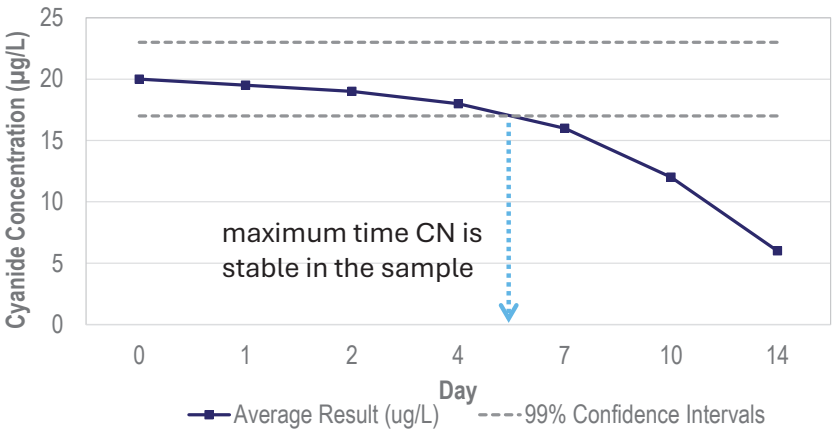
Designation: D 4841 – 88 (Reapproved 2018)

Standard Practice for
Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents[1]

CFR – Code of Federal Regulations. Part 136: Guidelines Establishing Test Procedures for Analysis of Pollutants

Study Approaches – Hold Time

- Hold Time Study
  - Collect a sample
  - Spike if necessary
    - Reanalyze over time – up to 14 days (standard sample hold time)
    - Calculate when CN is below the lower 99% confidence interval



Study Approaches - Interference

- Effluent-specific studies are required
- Assessing Interferences
  - Quench residual chlorine
  - Split samples (e.g., preserved and unpreserved)
  - Normal operating conditions
  - Rush analyses
- Lab / Method Variability
  - Low-level analyses
  - MS/MSDs at low concentrations
  - Splits to multiple laboratories

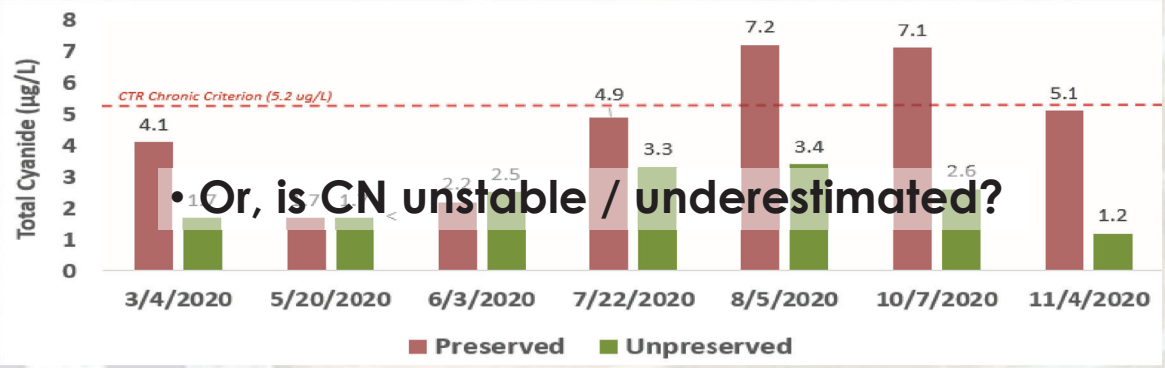
MS / MSD – matrix spike / matrix spike duplicate

Case Study – POTW 1

- Mid-Sized POTW
  - 5 MGD ADWF
  - Tertiary treatment
    - Primary clarifiers
    - Air-activated sludge basins (nitrification/denitrification)
    - Secondary clarifiers
    - Sand filtration
    - Chlorine disinfection with sulfur dioxide dechlorination
  - No industrial sources of CN

Case Study – POTW 1 (Phase 1)

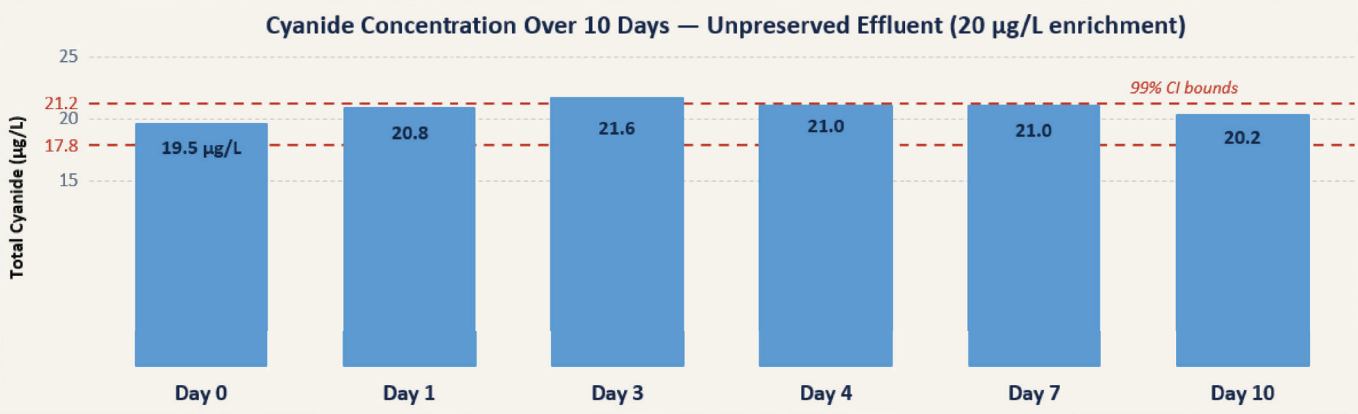
- Phase 1 Results



- Or, is CN unstable / underestimated?
- Unpreserved samples consistently below the CTR criterion.
- NaOH preservative interference can cause false positives

Case Study – POTW 2 (Phase 2)

- Phase 2 – Hold Time Study Results



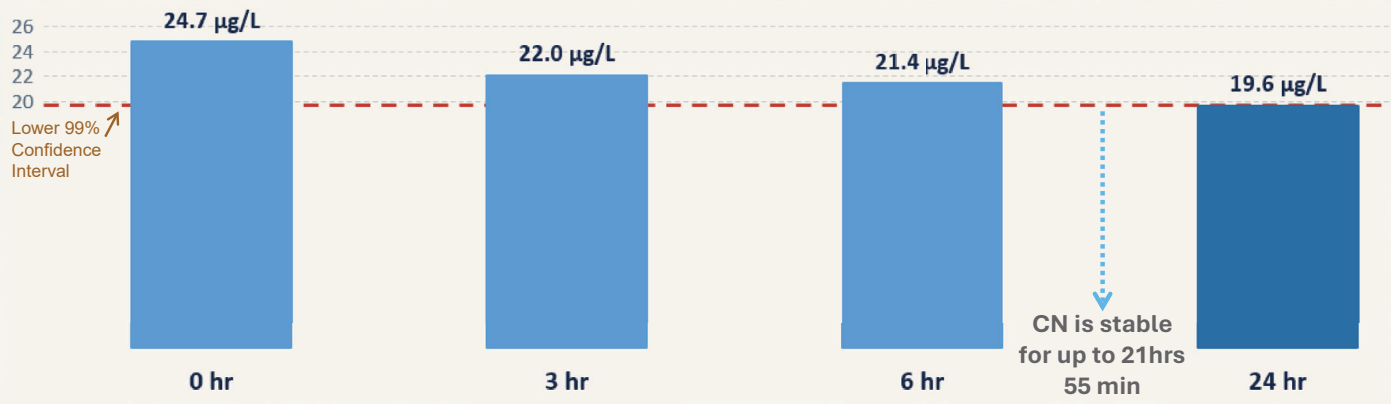
- Cyanide was stable in unpreserved final effluent for up to 10 days

Case Study – POTW 2

- Mid-Sized WWTP
  - 8.8 MGD ADWF
  - Advanced secondary treatment
    - Primary clarifiers
    - Anerobic digesters
    - Aeration basins
    - Secondary clarifiers
    - Cloth-media disk filters
    - Chlorine disinfection with sulfur dioxide dechlorination

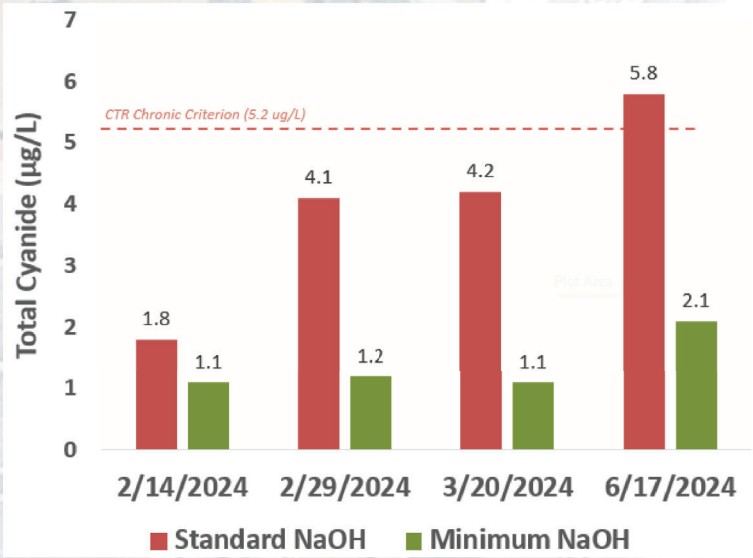
Case Study – POTW 2

- Phase 2 – Definitive Hold Time Study (per ASTM D4841)
  - CN stable in unpreserved effluent for up 21 hours and 55 minutes



Case Study – POTW 2

- Phase 3 – Assess Preservative
  - Minimum NaOH*
  - Standard NaOH in lab kit
- Standard NaOH > Min NaOH
- Standard NaOH results increased over time (64–282%)
- The City adopted sampling procedures to collect samples with minimal NaOH



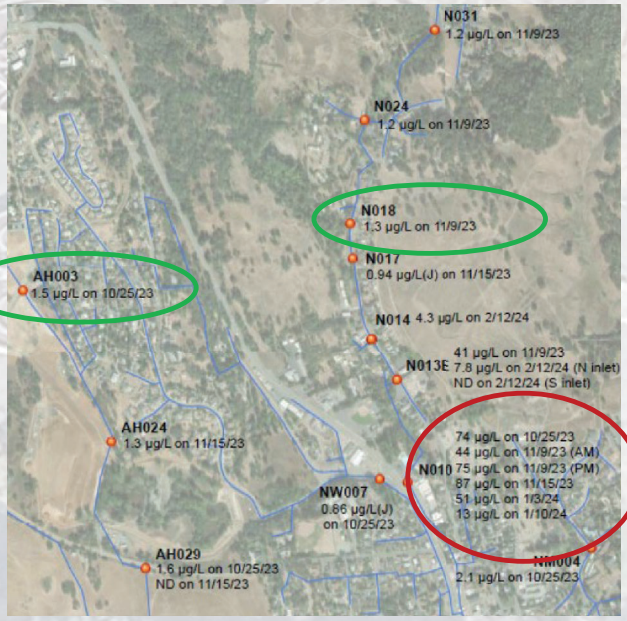
**Method is compliant with 40 CFR §136.3(e) if preserved within 15 minutes of collection*

Case Study – POTW 3

- Small WWTP
  - <1 MGD ADWF
  - Tertiary treatment
    - Oxidation ditches with nitrification/denitrification
    - Secondary clarifiers
    - Cloth disk filters
    - UV disinfection

Case Study – POTW 3

- Phase 4 – Sources
  - Don't discount collection system source(s)
- The City submitted an Infeasibility Analysis and was issued a Time Schedule Order by the Reginal Water Board
- Actions:
  - Control sources
  - Assess interferences



Summary

Analytical interferences are common with wastewater samples using acid distillation for total CN

NaOH is frequently the greatest cause of false positives

Regulations allow for methods to control interferences without an ATP

ASTM D7365 – Sampling Interferences

ASTM D4841 – Hold Time Studies

Identify false positives using split samples treated for interferences upon collection

Avoid false positives due to NaOH by

A) hold time study

B) minimize NaOH

C) free CN analysis

THANK YOU

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