

# Cyanide Analysis Essentials

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# Webinar survey – your feedback is appreciated!



The screenshot displays a webinar interface with several panels and callouts:

- Q&A (250 characters max)**: A text input field with a "Submit" button. A callout box says: "You can type your questions here anytime during the presentation."
- Slides**: The main presentation area showing a slide titled "Cyanide Analysis Essentials" by Craig Huff, Senior Technical Manager. A callout box says: "Gain access to the different resources."
- Resource List**: A sidebar menu with items: "DMR-QA Products", "DMR-QA Support", "DMR-QA FAQs", and "eDATA How-to Video: Change your Permittee Contact".
- Speaker Bio**: A panel for "Craig Huff", Senior Technical Manager at Waters ERA, with a "See Craig Huff Bio" link and a profile picture.
- Survey**: A panel titled "Webinar Survey - Thank you for attending!" with the text: "We value your feedback! Please take a few seconds to tell us how you feel about this webinar." A callout box says: "Please take a few seconds to fill out this survey, which will help us better understand your needs and improve our future webinars."
- Media Player**: A video player at the bottom showing a 0:00 duration.

# Cyanide Analysis

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- Key Learning Topics
  - Understanding different forms of cyanides and their environmental impact
  - Helpful hints and best practices
  - Benchmarking and improving laboratory practices
- Speaker – Craig Huff
  - Senior Technical Manager

## Outline

- Cyanides: Definitions
- Commonly Used Methods
- Helpful Hints- Distillation
- Helpful Hints- Analyses
- Valuable Insights and Lessons Learned
- PT Data Summary Statistics



# Cyanide Types of Environmental Concern

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Free  
Cyanide

Total  
Cyanide

Cyanide  
Amenable to  
Chlorination

Weak Acid  
Dissociable  
(WAD)

Available  
Cyanide

Reactive  
Cyanide



# Cyanide Definitions

- Free Cyanide
  - Simplest form to recover due to ease of reactivity
  - Highly toxic
  - Distillation typically not required to recover
  - Most common substrates used in environmental test methods are KCN or NaCN because they dissociate completely in water
  - Amenable to chlorination
  - KCN used in Waters/ERA WS PT Studies and WS CRMs

# Cyanide Definitions

- Total Cyanide
  - Applies to almost all types of cyanide (of environmental concern)
  - Requires a distillation step to recover complexed forms
  - $K_4Fe(CN)_6$  used in Waters/ERA WP / Soil PT Studies and WP / Soil CRMs due to stability and it also “tests” distillation effectiveness.
  - Post-distillation analytical techniques include:
    - Titrimetric
    - Colorimetric
    - Ion selective electrode (ISE)

## Cyanide Amenable to Chlorination

- Cyanide forms that decompose when chlorinated
- Includes some Weak-Acid-Dissociable forms as well as Free cyanides
- Many metal-complexed forms do not decompose under chlorination conditions
- Method requires two sample aliquots and distillations
  - One aliquot is treated (chlorinated) and distilled (Amenable CN)
  - The second aliquot is untreated and distilled (Total CN)
  - Amenable CN determined by difference (untreated minus treated)

Available Cyanide and Cyanide Amenable to Chlorination are essentially one and the same !

# Cyanide Definitions

- Weak-Acid-Dissociable Cyanide (WAD)
  - Operationally-defined analyte
  - Can include some forms of available cyanide
  - Requires a weak acid reflux (pH 4.6 – 6)
  - Can yield variable results even with a pure free cyanide source

# Cyanide Definitions

- Reactive Cyanide (SW-846 Method)
  - Operationally defined analyte defined under the Resource Conservation and Recovery Act (RCRA)
  - 40 CFR part 261.23— “Characteristic of reactivity...is a cyanide or sulfide bearing waste which when exposed to pH conditions between 2 and 12.5 can generate toxic gases, vapors or fumes in a quantity sufficient to present a danger to human health or the environment”.
  - Method is more complex and time-consuming
  - Can yield variable results
  - EPA withdrew this method in the late 1990s leaving labs “to their own devices” to determine method !

## Commonly used Methods

- SM 4500 CN-C (CN distillation)
- SM 4500 CN-D (Titrimetric)
- SM 4500 CN-E (Colorimetric)
- SM 4500 CN-F (ISE)
- SM 4500 CN-G (Amenable CN, with distillation)
- SM 4500 CN-H (Amenable CN w/o distillation)
- SM 4500 CN-I (WAD)
- EPA 335.4
- EPA 335.2
- EPA 9012 and 9014



## Helpful Hints

- Distillations
  - Obtain representative sample(s)
  - Ensure proper heating (rapid boil) without flooding condenser inlet !
  - “Midi-distillation” set-up works well and reduces waste
  - Ensure ~ 1-2 air bubbles/minute suction in boiling flask, helps prevent reverse flow of HCN through air inlet.
  - Thoroughly rinse scrubber tube, connecting tubing and combine rinses with scrubber solution flask
  - Test distillation effectiveness with a QC sample (CRM)
- SM 4500 CN...X contains very good information and is well organized.

## Helpful Hints

### ■ Analyses

- Freshly prepared reagents !
- Properly maintain equipment
- Ensure instrument calibration is accurate and linear
- Plot calibration data over time to detect changes in responses vs concentration (absorbances, slopes etc...)
- Utilize appropriate QC for the type of method you using
  - Ferro or Ferri CN sources to test distillation effectiveness
  - Try using a QC sample that contains a combination of Ferro or Ferri-CN and NaCN or KCN for Amenable CN (note: this solution performs best when made fresh and preserved with NaOH to pH of at least 12)
  - Incorporate CRMs in your routine analytical procedures...and monitor trends in their performance

## Valuable Insights & Lessons Learned

- Reporting PT Results
  - When submitting PT's, use the name and analyte code of the CN species stated on your accreditation certificate or permit; TNI analyte codes can help!
  - Know what the concentration ranges are for your PTs: Refer to TNI FoPT tables
  - Be aware of the PTRLs and ensure your method can achieve them
- Complex Interferences
  - Follow the guidance provided in your method to address matrix interferences
  - Matrix spikes are a valuable tool to assess the extent of any interferences
- Data Trending
  - Plotting/monitoring your Calibration and QC data are great indicators of potential quality issues— before they happen !

## Historical PT Data Summaries

- Represents thousands of data points and hundreds of studies
- WP
  - Total CN: Mean Recoveries = 99.2%
  - Precision: %RSD = 11.5%
  - Amenable/Available: Mean Recoveries = 105%
  - Precision: %RSD = 23.1%
- WS
  - Free & Total CN: Mean Recoveries = 99.6%
  - Precision: % RSD = 11.2%
- Soil
  - Total CN: Mean Recoveries = 70.1%
  - Precision: %RSD = 35.6%

Thank you!

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# Live Q&A Session: Cyanide Analysis Essentials

**Please submit your questions  
into the Q&A Chatbox**

<https://www.eraqc.com>