Bayer MaterialScience

Standard Practice D7365-09a for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide

NEMC

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Disclaimer

- This presentation serves to summarize ASTM Standard Practice D7365-09a and should not be construed as the advice or recommendation of myself or Bayer MaterialScience LLC.

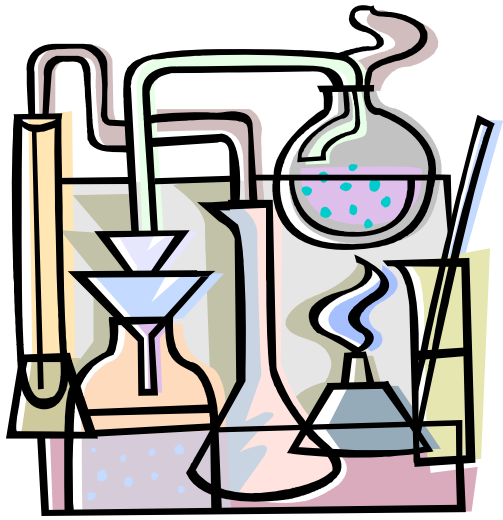
Why Develop a Standard Practice?

- If water samples are not properly preserved in the field, mitigated for interferences, and analyzed with appropriate analytical methods, significant positive or negative bias in the cyanide measurement is likely.
- Interference can lead to unnecessary permit violations or undetected cyanide discharges resulting in unnecessary fines or releases to the environment.
- Several cyanide methods have conflicting interference treatment techniques; some are outdated and do no reflect current technology
- Several questions raised during EPA Methods Update Rule (3/12/07)
  - 40 CFR Part 136.3, Table II Required Containers, Preservation Techniques, and Holding Times, Footnote 6
- Procedures are too complex for field personnel

ASTM D7365 Sampling / Mitigating Interference

- D19.06 assisted US EPA with Footnote 6 for Table II, 40 CFR 136.3
- D7365-07 published in 2007 in response to Methods Update Rule
- ASTM / EPA Workshop held June 2008 in Denver, CO
- Practice revised based on workshop, published as D7365-09
- Conducted Holding Time Study with ASTM Practice D4841
- Practice revised and published as D7365-09a
- Presented practice at 2009 NEMC in San Antonio, TX
- Proposed during recent EPA MUR to replace current footnotes

Potential Interferences



- Preservation with NaOH
- Sulfide and Sulfur
- Aldehydes (Formaldehyde, Acetaldehyde)
- Oxidants- Chlorine, Hypochlorite, etc.
- Sulfite, Thiosulfate, Thiocyanate
- Particulate Cyanide (e.g. Ferric ferro cyanide or Prussian blue)
- Carbonate
- Nitrate and Nitrite
- Unknowns

Sample Collection

- Containers and Volume
  - Amber glass or HDPE containers required unless total cyanide is the only parameter
  - Usually 1L sample; smaller volumes for flow injection methods
- Treat sample immediately upon sample collection using any or all of the techniques described in D7365 -09a
- Preserve immediately (within 15 minutes) after collection or treatment by adding 1mL 1M NaOH per L sample, then verify pH>10 with test strips

  - Be aware of potential issues with NaOH
  - Do not add NaOH if cyanide concentration will change
- Refrigerate samples (≤6°C)

Sodium Hydroxide Preservation Issues

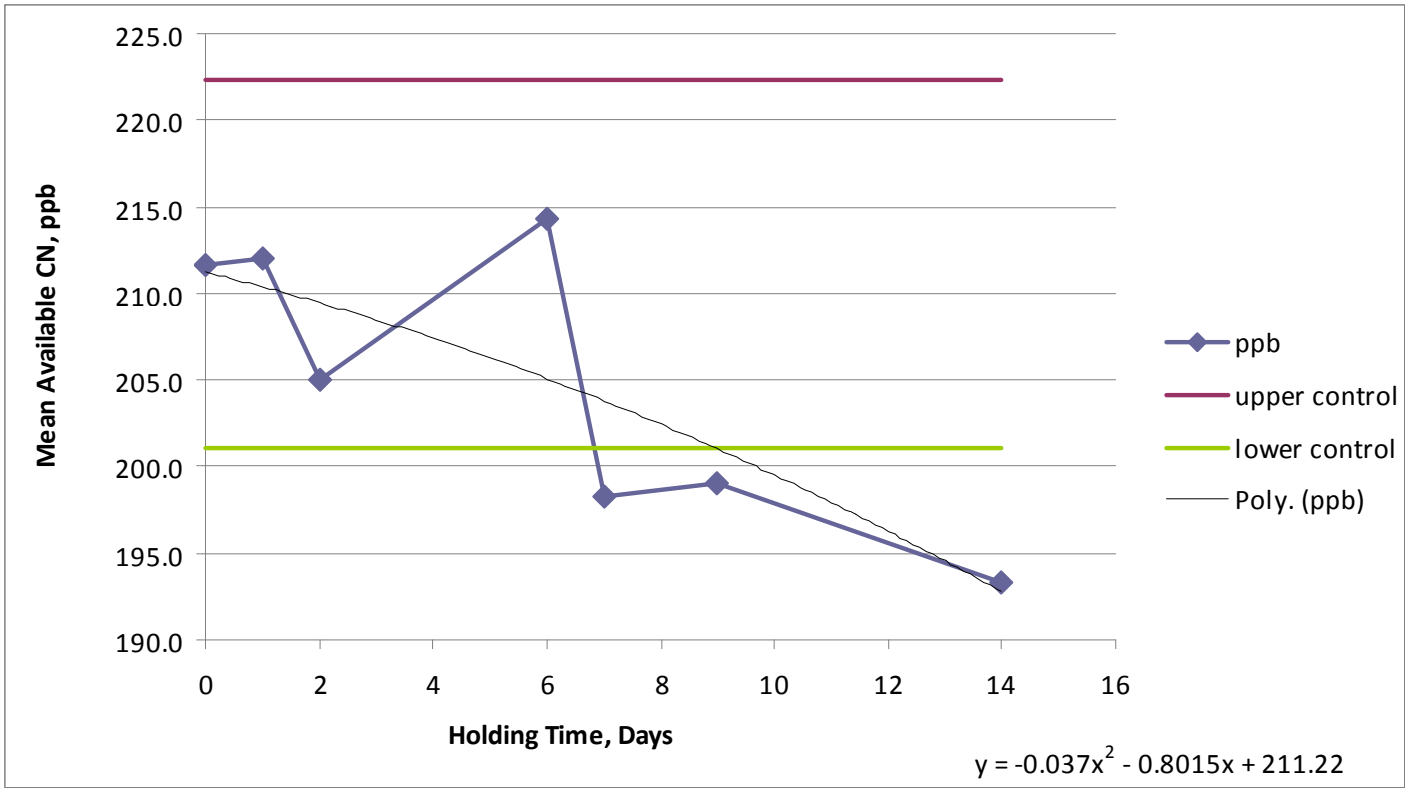
- Adding NaOH to samples containing formaldehyde, an ozone disinfection byproduct, can possibly result in cyanide formation during storage (ES&T, Vol. 41, 2007, Delaney, M.F. et. al.)
- Adding NaOH to samples containing thiocyanate in the presence of chloramines, which can form from ammonia and chlorine, can result in cyanide formation during sample storage.
  - Example: Increased cyanide concentrations occurred in public utilities agency samples immediately after adding NaOH.
- Adding sodium hydroxide to pH 12 in samples containing sulfite, a dechlorinating agent for wastewater treatment, can cause rapid cyanide degradation.
- Holding time study may be required

Holding Time Requirements

- Unless otherwise specified, samples must be analyzed within 14 days
- Certain matrices may require a shorter holding time or immediate analysis to avoid degradation
- Hold the sample no longer than the time necessary to preclude a change in cyanide concentration

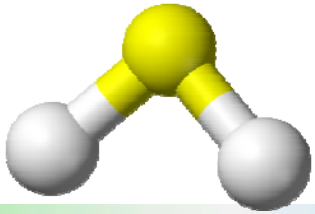
- A holding time study described in Practice D4841 is required if there is evidence that a change in cyanide concentration occurs from interferences which would cause the holding time to be shorter than specified

Example of Holding Time Study with D4841



Holding Time Evaluation of Challenge Matrix without NaOH Preservation, Available Cyanide Test Method D6888

Sulfide Mitigation



- Sulfide can cause positive or negative bias depending on the method
- Test for presence of sulfide during sample collection with lead acetate test strip previously moistened with acetate buffer.
  - Dark test strip indicates S^{2-} present > approximately 50 mg/L
- Dilute the sample(s) in the field with water so that test strip is negative. Preferrably, use a method with sulfide abatement such as D6888-09.
  - Record dilution factor for mathematical correction
- Sulfide can be precipitated with lead carbonate or lead acetate, but must be filtered immediately since this promotes the formation of thiocyanate. Only use this method if dilution cannot be performed.
- The task group has determined that cadmium chloride, volatilization and headspace expelling as described in Table II Part 136.3 are ineffective

Sulfur & Particulate Cyanides

- To remove elemental sulfur (S_8), immediately (within 15 minutes) filter the sample during sample collection
  - If the sample contains a significant (>1%) particulate matter or if particulate cyanides (e.g. ferric ferro cyanide or Prussian blue) are known or suspected to be present, save the solids for extraction
- If particulate cyanide is known or suspected to be present, stabilize the sample with NaOH during sample collection, then allow the sample to stand for at least 4 hours at room temperature prior to analysis
  - Prussian blue forms iron(III) hydroxide and ferrocyanide (soluble, brown)
  - Returns to blue color upon acidification in distillation flask
    - ASTM D7284-08 (MicroDist™) > recoveries than MIDI distillation
- If the sample contains significant particulate or solids, filter the solids then extract with 0.1M NaOH for separate analysis

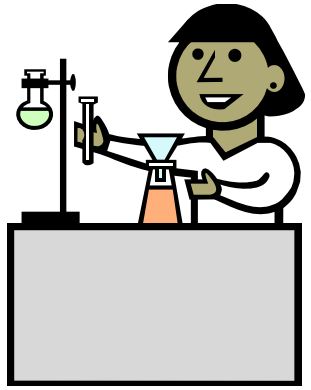
Aldehydes

- Low recovery or negative bias
  - If formaldehyde, acetaldehyde or other water-soluble aldehydes are known or suspected to be present, treat the sample with 2 mL 3.5% ethylenediamaine (EDA) per 100 mL of sample to avoid formation of cyanohydrins
    - Example: metals finishing effluent
    - EDA treatment effective up to 50 mg/L CH_2O
  - Samples can be screened for formaldehyde and other water-soluble aldehydes using test strips for formaldehyde or aldehydes
- Formaldehyde is suspected to cause cyanide formation during sample storage in preserved samples
  - Ozone disinfection

Oxidants

- Oxidizing agents can rapidly cause cyanide degradation
  - Add reducing agent only if an oxidant (e.g. chlorine) is known or suspected to be present
  - Screen samples for oxidizing agents with KI Starch paper (black paper is positive)
  - Unless specified otherwise, sodium arsenite is preferred
    - Other reducing agents-
      - Sodium thiosulfate (can cause interference)
      - Ascorbic acid (samples should be analyzed within 24 hours)
      - Sodium borohydride (if arsenic is present, toxic arsine gas can form)
  - If reducing agent is added, nitrite could possibly form which can contribute to positive interference during distillation
    - Add sulfamic acid during distillation to mitigate

Lab Responsibilities



- Upon receipt in laboratory
  - At a minimum, test for pH, sulfides, and oxidants using test strips
  - Document and mitigate any interference discovered
  - Recollect the sample if interference needs mitigated during sample collection
  - If re-sampling is not possible, qualify the data
- Mitigate interferences as necessary during analysis
  - Use appropriate analytical methods

Sulfite, Thiosulfate or Thiocyanate

- Sulfite or thiosulfate can cause low cyanide recoveries with distillation and colorimetry methods
- Thiocyanate can decompose into cyanide and sulfide during distillation or UV digestion, especially if oxidizing agents such as NO_3 are present
- Colorimetric methods are susceptible to positive bias from thiocyanate even in the absence of oxidizers
- If sulfite, thiosulfate or thiocyanate are known or suspected to be present use appropriate method to minimize interferences
  - D6888 shows least amount of interference (Available Cyanide)
  - D7284 or D7511 with antioxidant (Total Cyanide)
  - Avoid distillation or UV with colorimetric determinative step

ASTM D19 Cyanide Challenge Matrix

- Reproducible matrix for interlaboratory study
  - D7237 (Aquatic Free Cyanide)
- Based on precious metals mining process water
  - 25 mg/L NH_3 as N, 25 mg/L NO_3 as N, 475 mg/L SO_4

    25 mg/L OCN and 15 mg/L SCN
- Positive interference for total cyanide (distillation)
  - SCN and NO_3 (oxidizer) forms CN^-
    - Average observed interference = 62 ug/L as CN^-
- No positive interference for free cyanide or available cyanide
  - D7237 and D6888
  - No distillation or digestion required
    - gas diffusion separation with amperometric detection

Antioxidants to Mitigate NO_3 with Thiocyanate

Sample Matrix	Matrix Spike	D7284-08 Pretreatment	D7511-09 Alternate Acid
Sample / Description	200 ug/L as CN^-	Ascorbic Acid Added to Samples Prior to Distillation	Ascorbic Acid & Citrate in TA1 instead of H_3PO_2
Control	None	<5	<5
	KCN	161	200
	$K_3Fe(CN)_6$	191	158
200 mg/L S_2O_3	None	<5	9.66
	KCN	Sample Lost	229
	$K_3Fe(CN)_6$	190	169
200 mg/L SO_3	None	<5	5.82
	KCN	176	200
	$K_3Fe(CN)_6$	187	164
200 mg/L SCN	None	<5	42.3
	KCN	146	256
	$K_3Fe(CN)_6$	154	208
Challenge Matrix	None	<2	<5
	KCN	156	208
	$K_3Fe(CN)_6$	181	170

Carbonate

- Carbonate interference is evidenced by effervescence or foaming from the release of CO_2 upon acidification
  - Causes negative bias or irregular peak shapes (amperometry) when greater than 1500 mg/L
  - To avoid interference, add calcium hydroxide to pH 12-12.5 or until a precipitate forms during sample collection (preferred) or in the laboratory if sample has already been preserved with NaOH
  - Removes insoluble cyanide complexes, which can partially be recovered with dilute acetic acid rinses to the filter
  - Calcium hydroxide treatment may reduce cyanide recoveries
  - Alternatively, dilute as necessary to minimize interference

Nitrate-Nitrite

- For total cyanide by distillation, nitrate or nitrite can react under conditions of the distillation with other contaminants to form cyanides, resulting in positive bias
  - For D2036 and D7511, add sulfamic acid prior to acidification as directed in the test methods, recommended for all samples.
  - Do not add excessive sulfamic acid as this could result in method bias
  - If reducing agents were added to de-chlorinate or to remove oxidizers, add ascorbic acid during distillation

Quality Control

- Report cyanide as CN^- (usually in ug/L) and correct for any dilutions
- Make note of any specific interference and treatment
- If the mitigating interference technique is not described in D7365, provide reference or supporting data to justify the action
- Follow all QC requirements in method and perform MS/MSD to evaluate precision and recovery for unknown matrices
  - Acceptable recoveries DO NOT rule out interference
- Sample characterization may be necessary to identify and mitigate interferences

Acknowledgements

- ASTM D19.06 Cyanide Task Group
- US EPA Office of Water

Thank you for your attention!