Cyanide Analysis and the CNSolution 3100

Sales

William Lipps
OI Analytical

O·I·Analytical
A World of Solutions

History, Sources, and Uses of Cyanide

O·I·Analytical

Mining is not the major source of cyanide pollution

- Automobile exhaust (single largest source of HCN pollution)
  - 95% of atmospheric cyanide
- Cigarette smoke
- Burning of plastic (house fires, etc.)
- Road salt
  - 95 % of surface water contamination

CN

NH_3

PO_4

NO_3

O·I·Analytical

Cyanide has been used in industry for over 100 years

- 13 % Mining
- 87 % other stuff

- Products produced from cyanide are used by millions of people every day

CN

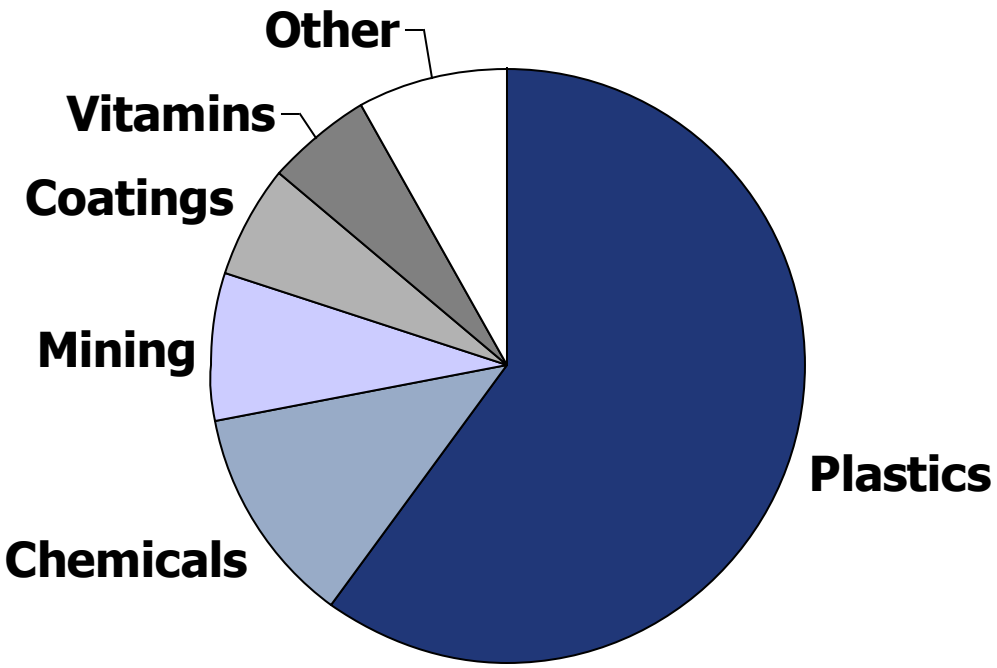
NH_3

PO_4

NO_3

O·I·Analytical

Distribution of the Industrial Uses of CN



O·I·Analytical

Industries that use cyanide in their processes and may need to monitor it

- Electroplating
- Pharmaceuticals
- Metallurgy
- Jewelry
- Photography
- Precious Metal Extraction
- Computer electronics
- Adhesives, dyes, nylon, paint
- Road salt and table salt

Industrial Facilities with Cyanide-Bearing Waste Streams

- Petroleum Refineries
- Coal-fired Power Plants
- Mining/Precious Metal Operations
- Wastewater Treatment Plants
- Semiconductor Manufacturing

If you burn organics cyanide is there!

O·I·Analytical

Demand for Cyanide Methods

O·I·Analytical

Who is measuring cyanide?

- **NPDES and pretreatment permit holders**
  - **Combustion process**
  - **Electroplating**
  - **Aluminum manufacture**
  - **Plastics and adhesives**
  - **Pharmaceutical (ibuprofen and naproxen)**
  - **POTW**
- **SDWA compliance monitoring**
  - **Regulated as free cyanide**
- **Combustion gases and industrial hygiene**
- **Adulterated foods and beverages**

Who requires cyanide testing?

- **Regulatory Agencies**
  - **USEPA**
    - **CWA (priority pollutant)**
    - **SDWA (primary contaminant)**
  - **States**
    - **CWA**
    - **SDWA**
  - **OSHA**
- **Industrial or Municipal laboratories**
  - **Self Monitoring**
  - **Process control**

O·I·Analytical

Safe Drinking Water Act (SDWA) compliance monitoring

- **Regulated Parameter is “free” cyanide**
  - **See references in OI brochure**
- **OIA1677-DW or ASTM D6888-04**
  - **Only methods that run “free” cyanide**
  - **Total is “screening”, must run CATC if detected**
- **Direct colorimetry does not work**

Use configuration 1 for SDWA compliance monitoring

O·I·Analytical

NPDES and pretreatment permits regulate available or total cyanide

O·I·Analytical

Total Cyanide is by far the most common cyanide measured worldwide

- **Most use manual distillation.**
  - **Prolonged heating (125 °C) , strong acid (pH <2) breaks apart most CN complexes.**
  - **HCN carried by purge gas and collected in a basic absorber solution.**
  - **CN in the absorber is measured by colorimetry, ISE, or titration.**

O·I·Analytical

The mindset that manual distillation is best is a major obstacle

- **Manual distillation / colorimetry is perceived as highly accurate**
  - **EPA has acknowledged flaws since 1980's**
- **Manual distillation considered cost effective for a few samples**
- **Manual distillation is EPA approved**
  - **Wastewater (40 CFR Part 136)**
  - **NOT SDWA (only screening for SDWA)**

The approved manual distillation / colorimetry methods are:

- EPA 335.4
- SM 4500
- ASTM D2036
- Lachat

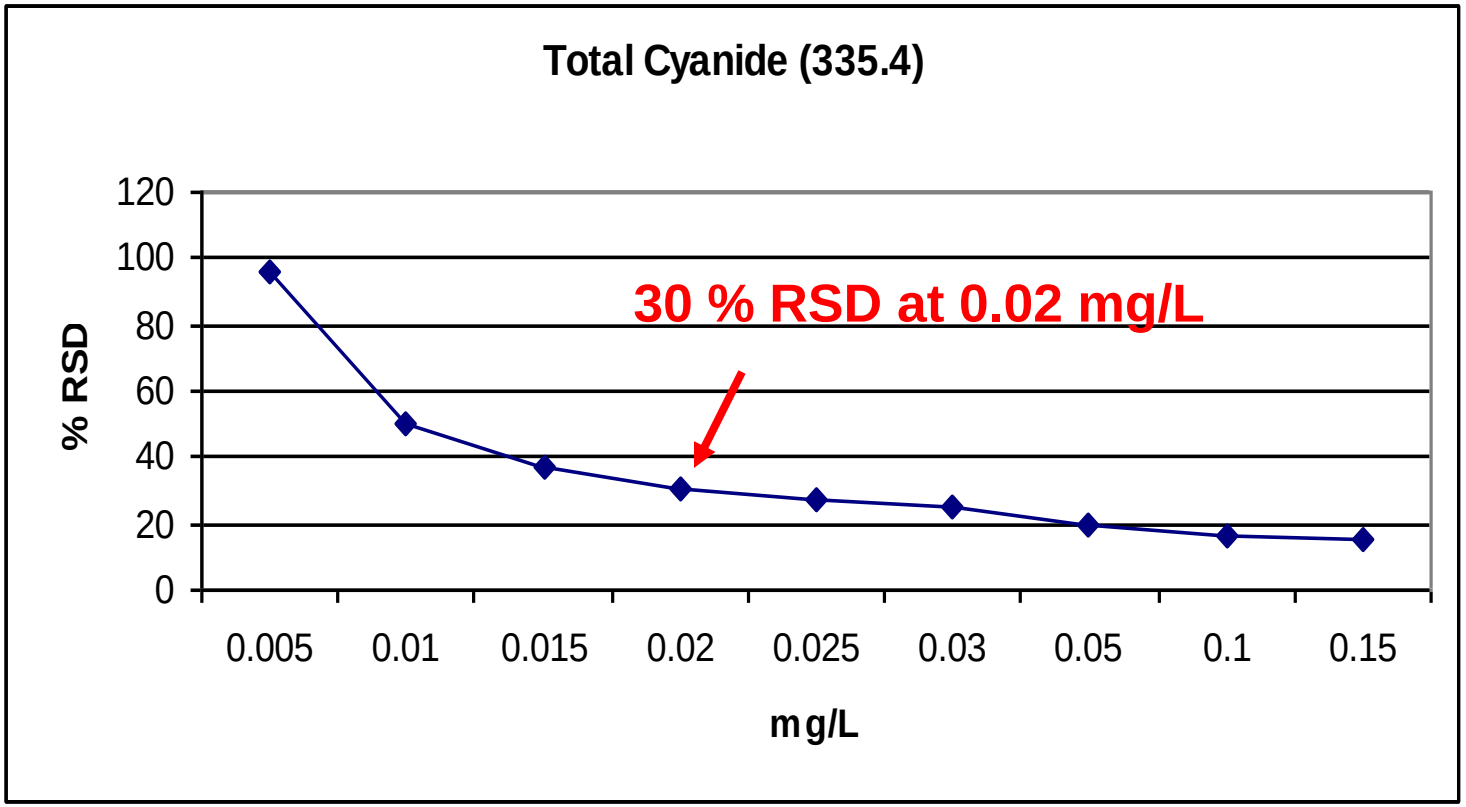
- EPA and ASTM allows Lachat Microdist and Midi dist
  - SM 4500 does not

O·I·Analytical

Even though the distillation is manual, the analysis is automated (usually)

- EPA 335.4
  - Manual distillation
  - CFA using pyridine barbituric acid
- ASTM D2036
  - Manual distillation
  - CFA or manual colorimetry, ISE
    - Changing in 2010
- Lachat
  - Manual distillation (MicroDist)
  - FIA using pyridine barbituric acid
- SM4500
  - Manual distillation (Macro)
  - Manual Colorimetry

The real life detection limit of manual distillation is higher than reported



100 % RSD at 0.005 mg/L

O·I·Analytical

Why do we measure “total” cyanide?

- There were no other methods in the late 1970’s
- A law suit
- Total measures “all” species
  - Iron cyanides
  - Available cyanide
  - Free cyanide

O·I·Analytical

Problems with Distillation Based Cyanide Methods

- Low repeatability and reproducibility (distillation precision and accuracy are operator-dependent).
- Multiple interferences.
- Time consuming and labor intensive sample preparation.
- Glassware requires lots of manipulation, Microdist $7.00 per tube.

CN

NH_3

PO_4

NO_3

O·I·Analytical

Distillation-believed to separate cyanide from interferences causes most of them

- In samples of well known and/or simple matrices, distillation is adequate.
- Real samples are never simple matrices
- On-line UV distillation methods are worse than manual distillation.

CN

NH_3

PO_4

NO_3

O·I·Analytical

The predominant interferences with distillation are:

- Thiocyanate
- Thiocyanate + Nitrate
- Thiosulfate
- Sulfite
- Sulfide

Thiocyanate is a significant interference

- Thiocyanate is present in almost all wastewaters (1.0–50 mg/l normal)
- Interferences can be both positive (CN created) or negative (CN destroyed)
- There are no “spot” tests to determine thiocyanate

Thiocyanate plus nitrate is a positive interference

SCN^- (mg/L)	NO_3^- (mg/L)	CN^- (mg/L)
0.100	1.00	Not Detected
0.100	10.0	0.010
0.100	25.0	0.017
0.100	50.0	0.060
0.100	100	0.086
1.00	10.0	0.009
1.00	50.0	0.038

Use the ASTM “challenge matrix” as ammunition – suggest it be run!

Method	ppb CN detected
EPA 335.4	50 - 60
Lachat online dist	More than 1000
Kelada 01	500 – more than 1000
ISO 14403	900
ASTM D7511	0 - 30
OIA1677	0

O·I·Analytical

All sulfur compounds except sulfate interfere during distillation

- **Elemental Sulfur**
  - $8CN^- + S_8 \rightarrow SCN^-$
- **Metal Sulfides (distilling with solids present, or if sulfide complexing metals are added to distillation flask)**
  - Cu_2S, FeS, PbS, $CuFeS_2$, CdS, ZnS, etc.
  - S reacts with CN^- to form SCN^-
- **Thiosulfate**
  - $CN^- + S_2O_3^{-2} \rightarrow SCN^- + SO_3^{-2}$
- **Sulfite**
  - $Na_2SO_3 + O_2 + CN^- \rightarrow OCN^- + Na_2SO_4$

Sulfur compounds will be in almost every sample

- Sulfide is everywhere
- Thiosulfate used to de-chlorinate samples
- Sulfite used to de-chlorinate effluents

Interferences in Current Cyanide Methods

- Determinative Step
  - Titration
  - ISE
  - Colorimetric
  - Amperometric

Interferences – Determinative Steps

- Titration
  - Titration of Cyanide with Silver Ion
  - Many references consider this to adequately measure free cyanide.
  - Interferences
    - Sulfide
    - Phosphate
    - Arsenate
    - Excess Chloride

Interferences – Determinative Steps

- Ion Selective Electrode (ISE)
  - Found in many test kits
  - Interferences are:
    - Sulfide
    - Silver
    - Bromide
    - Copper
    - Mercury
    - Lead
    - Thallium
    - Excess Chloride

Interferences – Determinative Steps

- Colorimetric Methods
  - Usually Pyridine-Barbituric Acid
  - Interferences are:
    - Thiocyanate
    - Sulfide
    - Cyanogen Chloride
    - Reducing Agents
    - Color, turbidity, and high salinity

Interferences – Determinative Steps

- Amperometric Detection
  - Sulfide and mercaptans

Sampling and Preservation

- Traditional sample pretreatment don't work.
- ASTM D19.06 developed D 7365-07 *standard practice for sampling, preservation and mitigating interferences in water samples for the analysis of cyanide.*
- This is a "living" document and will change as new discoveries are made.

Sampling and Preservation

- The ASTM guide is recommended for use with all total cyanide, available cyanide, and free cyanide methods.
- The guide addresses known interferences and holding times.

Sampling for Cyanide – No Known Interferences Present

- Basic instructions:
  - Collect enough sample for the required analysis in clean amber glass containers.
  - No sulfide detected by lead acetate test strips (<50 ppm).
    - Adjust the pH to 12 with NaOH and analyze within 48 hours.
    - Perform matrix specific holding time study to verify samples can be held longer than 48 hours without further treatment.

Sampling for Cyanide – Sulfide Present

- To extend holding time and treat interferences (total and available CN).
  - Sulfide – positive to lead acetate paper (>50 ppm).
    - **Dilute** sample so that sulfide is no longer detected.
    - Record dilution factor.
    - Adjust to pH 12 with NaOH.
    - Ship to laboratory.
    - Analyze within holding time (14 days?).

Sampling for Cyanide – Sulfide Present

- Sulfide > 50 ppm – analysis for aquatic free cyanide **only.**
  - Adjust pH to 11 with NaOH.
  - Add 1 mg of powdered cadmium chloride per milliliter of sample.
  - Cap and shake container to mix.
  - After precipitate settles recheck with lead acetate paper.
  - Treat again if necessary.
  - Filter, refrigerate, and ship to laboratory.

Rationale – Sulfide Treatment

- Tests were made using an ASTM draft total cyanide method based on distillation followed by GD-amperometry.
- Available cyanide was determined by ASTM D6888-04.

Traditional Treatments for Sulfide 200 ppm S added

Addition of powder followed by filtration in < 2 minutes.
200 ppb CN as KCN added.

Chemical Treatment	**Avail. CN ug/L D6888-04**	**% Rec**
Cadmium Carbonate	>2000	> 1000
Bismuth Nitrate	>2000	**>1000**
Lead Acetate	149	74.5
Lead Carbonate	>2000	**>1000**

O·I·Analytical

Traditional Treatments for Sulfide 200 ppm S added

Addition of powder followed by centrifugation and filtration in < 15 minutes. 200 ppb CN as KCN added.

Chemical Treatment	**Avail. CN ug/L D6888-04**	**% Rec**
Cadmium Carbonate	193	96.5
Cadmium Chloride	181	90.5
Lead Acetate	66.9	**33.5**
Lead Carbonate	153	76.5

O·I·Analytical

Precipitation of Sulfide With Cadmium 200 ppm S added

CN Species	Avail CN ug/l	% Rec	Tot CN ug/l	% Rec
KCN	197	98.5	NA	NA
Ferric CN	NA	NA	2.66	**1.33**
Mercury	44.6	**22.3**	45.5	**22.8**
Nickel	176	88	165	82.5

O·I·Analytical

Addition of Bismuth (Method 9010) 200 ppm S added

CN Species	Total CN ug/l	% Rec
KCN	327	164
Ferric CN	267	134
Sulfide only	209	NA

Bismuth added to distillation flask according to method

Addition of Bismuth to Samples 200 ppm S added

CN Species	Total CN ug/l	% Rec
KCN	199	99.5
Ferric CN	101	50.5
Sulfide only	26.6	NA

Sulfide precipitated from sample then filtered prior to distillation.

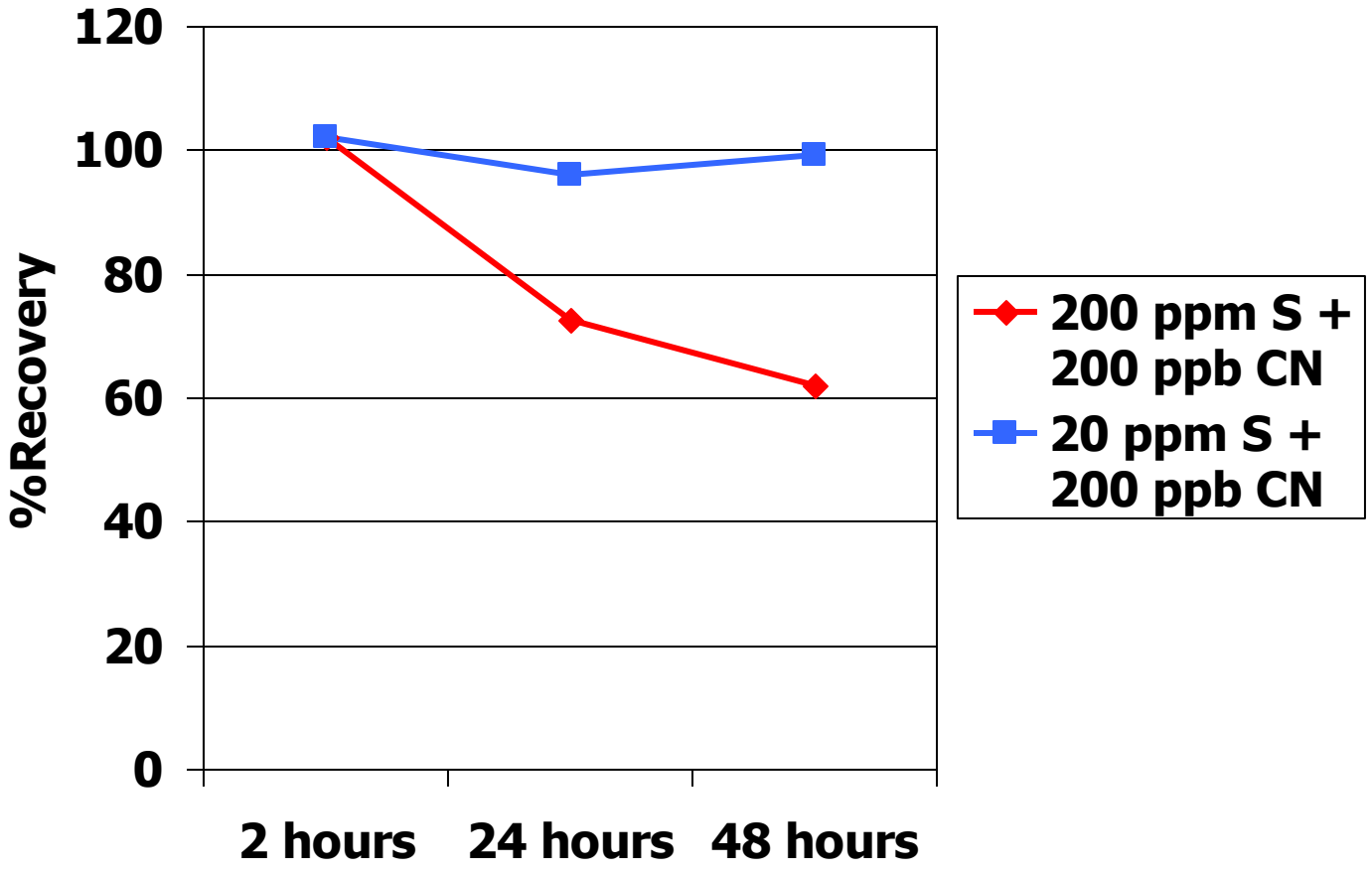
O·I·Analytical

Sulfide Removal – Headspace or Dynamic Stripping

CN Species	Avail. CN ug/l	% Rec
KCN	144	71.8
Nickel CN	168	83.8
Mercury CN	142	70.8

Detectable Sulfide was still present after treatment. Recoveries seem acceptable but detectable sulfide will lower cyanide over time.

Holding Time Study – Sulfide bearing samples.

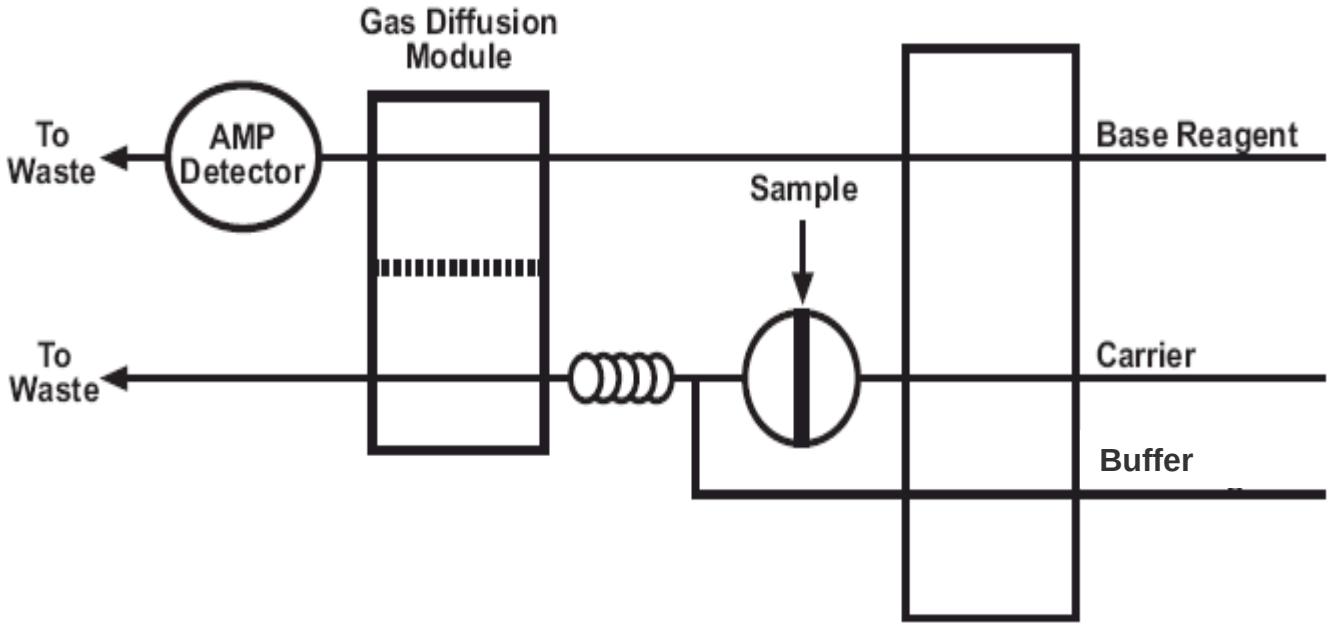


O·I·Analytical

Summary of Sulfide Treatments

- Precipitation – low recoveries
- Headspace/Dynamic stripping – low recoveries and sulfide still present.
- Dilution is the Solution – the only real way to guarantee no interferences from sulfide is to dilute it out and run sample within 48 hours.

Free Cyanide Method



CN

NH_3

PO_4

NO_3

O·I·Analytical

Weak and Dissociable Cyanide

- Transition metals form complexes (not ionic bonds) with Cyanide.
- Transition metals that form “weak” complexes will release CN as HCN at a pH of about 4.5.
- Examples of “weak” complexes are:
  - $Ag(CN)_2$, $Hg(CN)_2$, $Cu(CN)_4^{-2}$,
  - $Cd(CN)_4^{-2}$, $Zn(CN)_4^{-2}$, $Ni(CN)_4^{-2}$

O·I·Analytical

WAD Cyanide - SM 4500-CN-I

- Defined as the amount of HCN released by distillation at pH 4.5.
- The HCN released is absorbed into a solution of sodium hydroxide and determined colorimetrically with pyridine-barbituric acid reagent.
- WAD *really* stands for Weak and Dissociable, but is now called Weak Acid Dissociable.

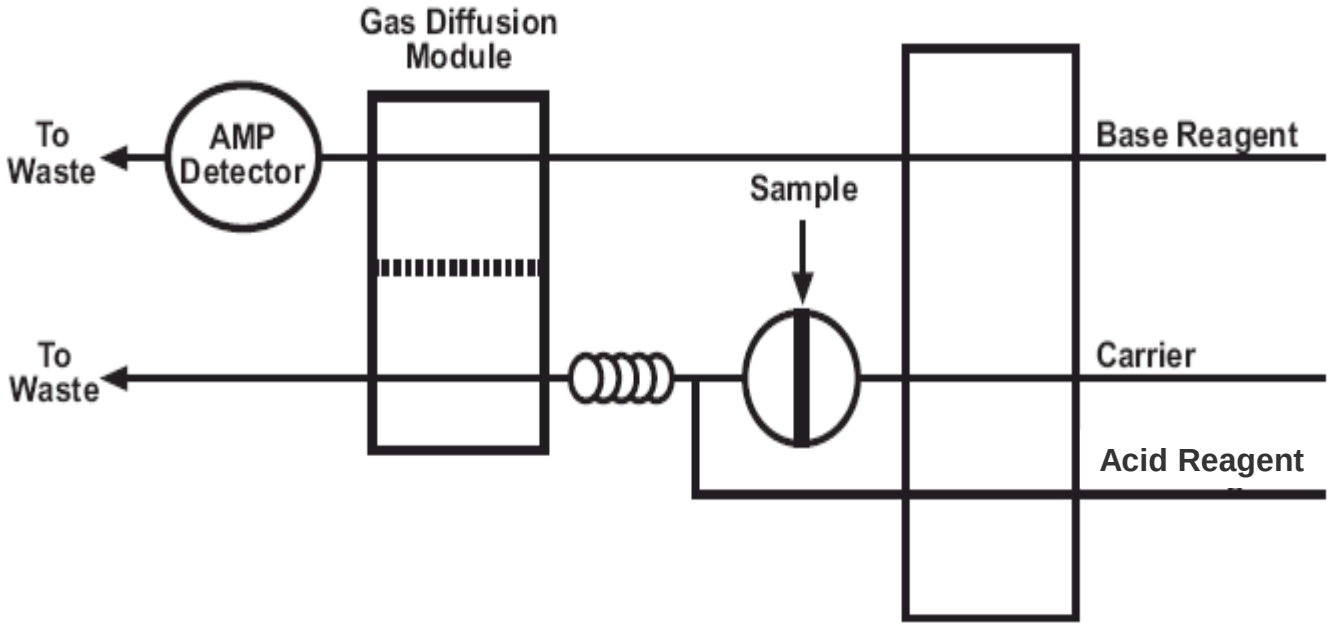
Cyanide Amenable to Chlorination (CATC)
SM 4500-CN-G, ASTM D2036

- Similar Cyanide species recovery as the WAD method.
- This method requires samples be split into two portions.
- One half is chlorinated, and the other half is not.
- Both are distilled according to the “total” cyanide method, and the difference is Amenable Cyanide.

Available Cyanide – OIA 1677, ASTM D6888

- Flow injection – gas diffusion with amperometric detection (no distillation).
- Same species as CATC or WAD, but with higher recoveries at higher concentrations.
- Measures free cyanide and weak acid dissociable cyanide.
- Does not measure strong metal cyanide complexes (iron cyanides).
- Ligands are added for complete recovery of Ni and Hg cyanide.

OIA 1677 and ASTM D6888



CN

NH_3

PO_4

NO_3

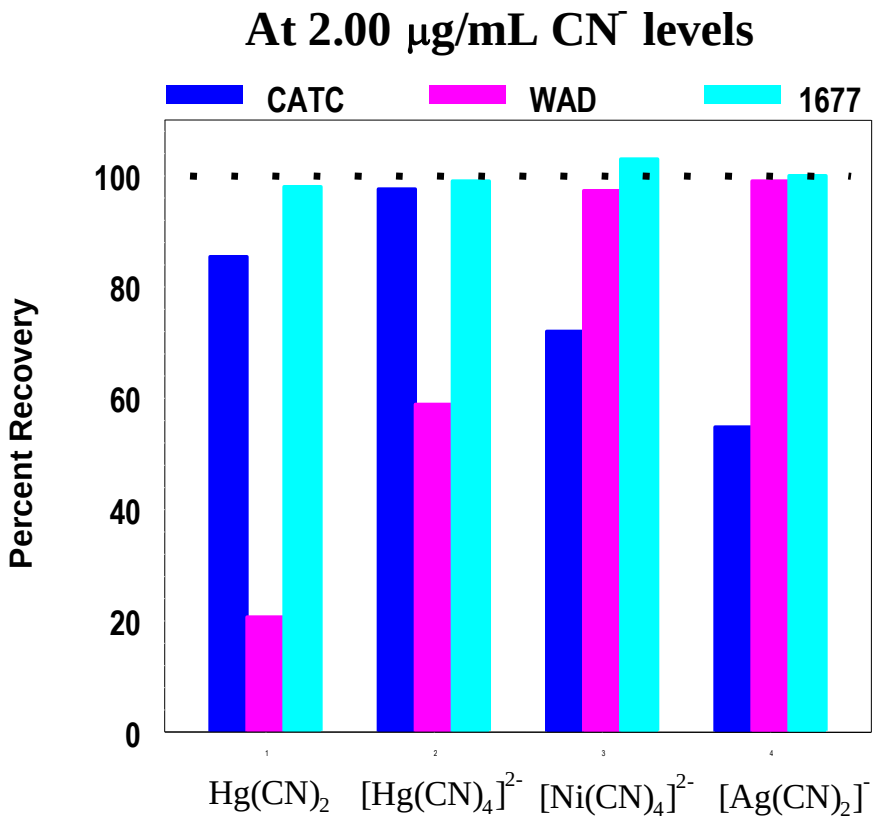
O·I·Analytical

OIA Method 1677 and ASTM D6888

- Complete Recovery
  - CN^-
  - HCN^-
  - Zn Complexes
  - Cd Complexes
  - Ag Complexes
  - Ni Complexes
  - Hg Complexes
- No Recovery
  - Ferrous Complexes
  - Ferric Complexes
  - Gold Complexes
  - Cobalt Complexes
  - Thiocyanate

O·I·Analytical

Comparison of "Available CN Methods"



Possible Interferences with GD-FIA methods

Ion	CN^- Found (mg/L) Ratio Ion/CN^- = 100	CN^- Found (mg/L) Ratio Ion/CN^- = 1,000
NH_4^+	0.200	0.202
OCN^-	0.200	0.202
SCN^-	0.200	0.204
$S_2O_3^{-2}$	0.205	0.204
Cl^-	0.201	0.200
Br^-	0.197	0.202
I^-	0.205	0.203
CO_3^{-2}	0.198	0.197
NO_2^{-2}	0.200	0.202
NO_3^{-2}	0.197	0.202

* All samples at 0.200 mg CN^-/L

O·I·Analytical

Advantages of OIA 1677 and D6888 for the Determination of Available CN

- Complete cyanide recoveries from all complexes that produce “available cyanide”.
- Cyanide recoveries are concentration independent.
- Dynamic range of 0.002–5.00 mg/L CN in a single calibration. (D6888 0.002 – 0.400 mg/l).
- No cyanide recoveries from strong metal complexes.

Advantages to OIA 1677 and D6888 for the Determination of Available CN (cont.)

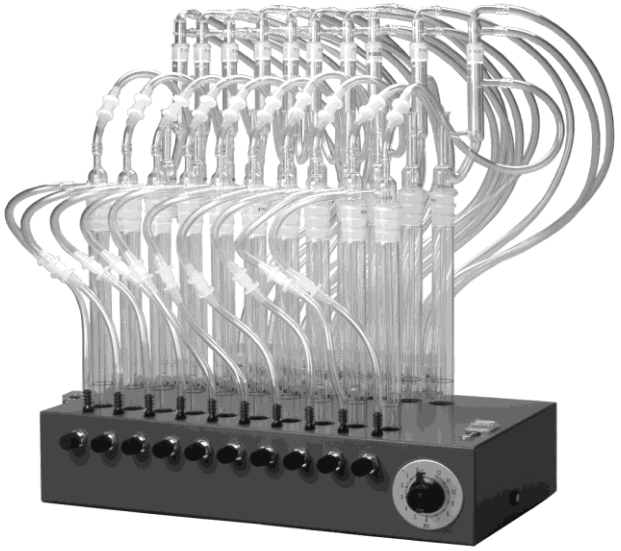
- Total analysis time is about 2 minutes per sample (compared to hours by distillation).
- Limit of detection of 0.0005 mg/L CN or lower.
- Few known interferences.
- Less than 1 mL of sample is required per analysis (compared to 50–500 mL by distillation).

Proposed Total Cyanide Method

- ASTM draft method for total cyanide in water by manual distillation followed by gas diffusion – amperometric detection. (OIA 1677 or ASTM D6888)
- The method will be submitted for ballot in 2007, and is expected to be accepted for NPDES reporting once approved by the ASTM.
- This method eliminates the need for the pyridine-barbituric acid reagent.
- MDL = 0.003 mg/l on ferric cyanide complexes.
- The method produces accurate results in samples that are problematic with EPA 335.2 and 335.4.

WAD, CATC, and Total CN Distillation

Macro Distillation



MIDI Distillations

O·I·Analytical

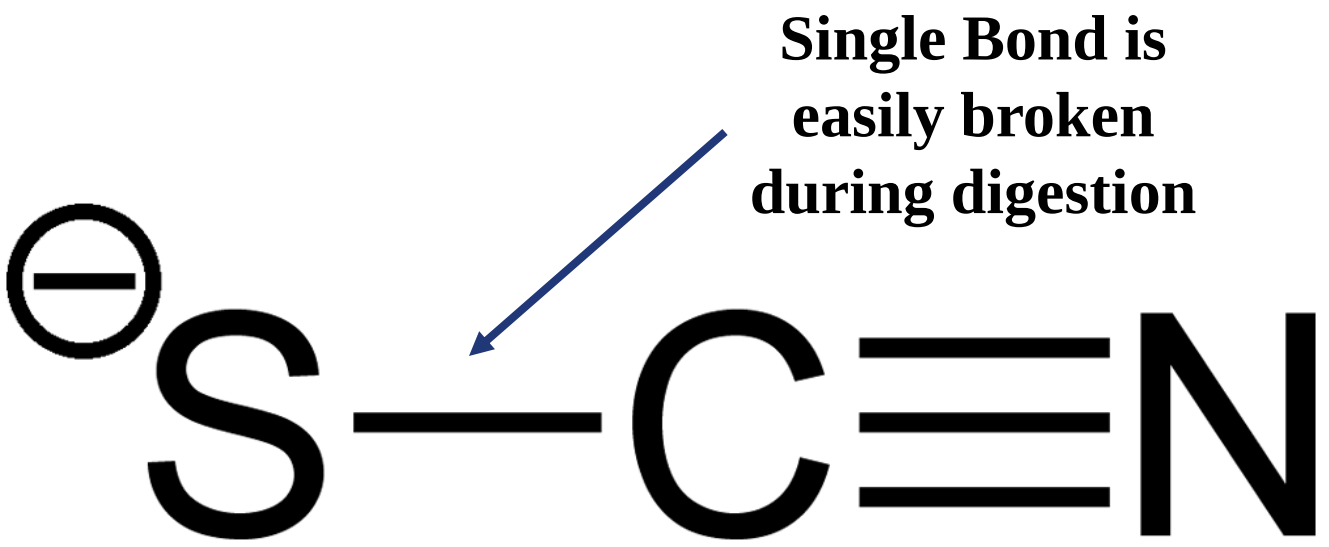
Current Cyanide Methods

ASTM D7237	Free Cyanide
SM 4500-CN-G, ASTM D2036	Cyanide Amenable to Chlorination (CATC)
SM 4500-CN-I	Weak Acid Dissociable (WAD)
OIA 1677, ASTM D6888-04	Available Cyanide *
EPA 335.2, 335.4, ASTM D2036	Total Cyanide

*** EPA Approved Non-Distillation Methods**

O·I·Analytical

Interferences – Thiocyanate



Removal of Chlorine

"Total" Cyanide

- "Total" Cyanide is operationally defined as the amount of HCN liberated by distillation from a $MgCl_2$/Sulfuric Acid Solution (>100 °C, pH < 1).
- The HCN is absorbed into a sodium hydroxide solution and measured, usually Colorimetrically.
- By Definition, Total Cyanide does NOT include Thiocyanate or Cyanate

Distillation Free Total Cyanide

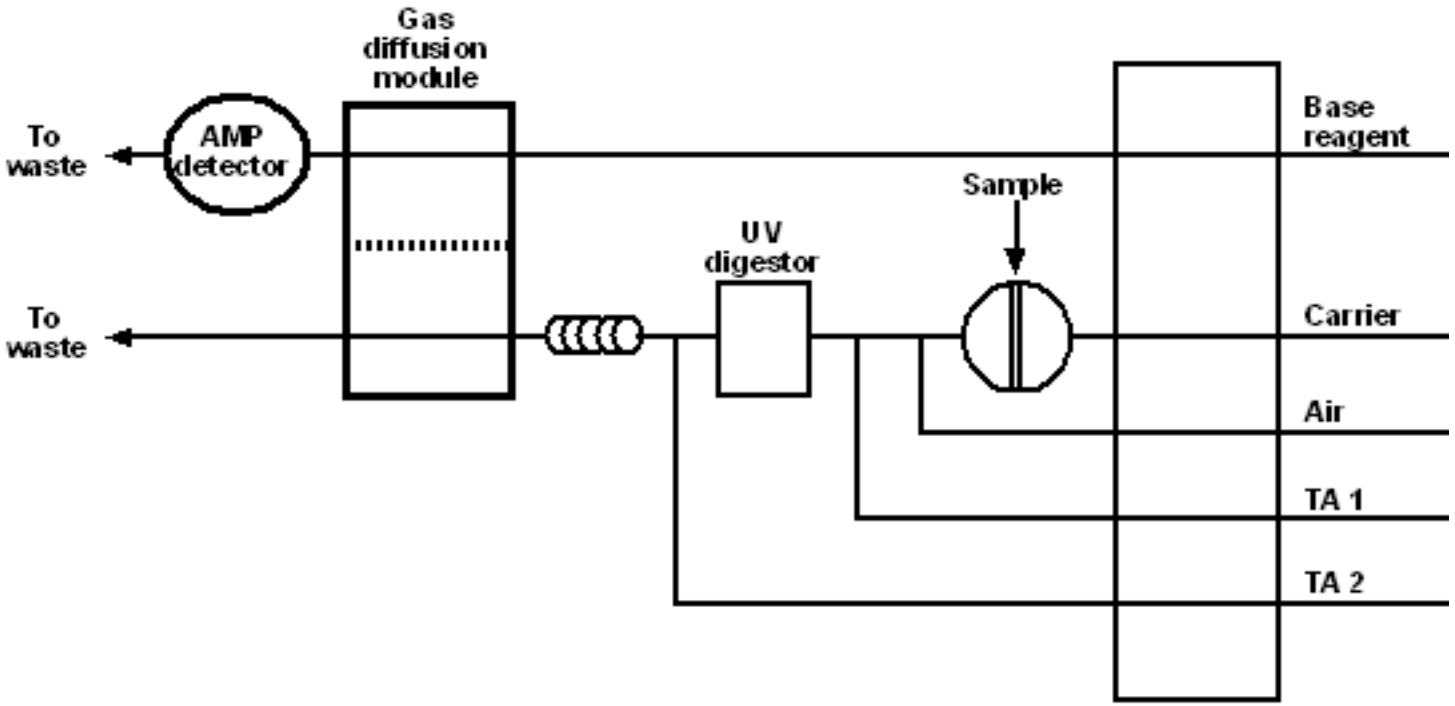
- Draft method at ASTM
- Based on OIA Method 1677 and ASTM D6888 Ligand Exchange Flow Injection-Gas Diffusion Amperometric methods for determination of Available Cyanide.
- Instead of ligands, metal cyanide complexes are “broken up” by UV irradiation.
- The method quantitatively determines the same cyanide species as “total” cyanide by distillation.
- Results are obtained in minutes instead of hours.

O·I·Analytical

Why a Non-Distillation Method?

- Distillations are time-consuming.
- Distillation has a limited throughput.
- Distillation, though designed to separate cyanide from interferences, actually increases them.
- Cyanide measurements without distillation are more accurate.

Total Cyanide without Distillation

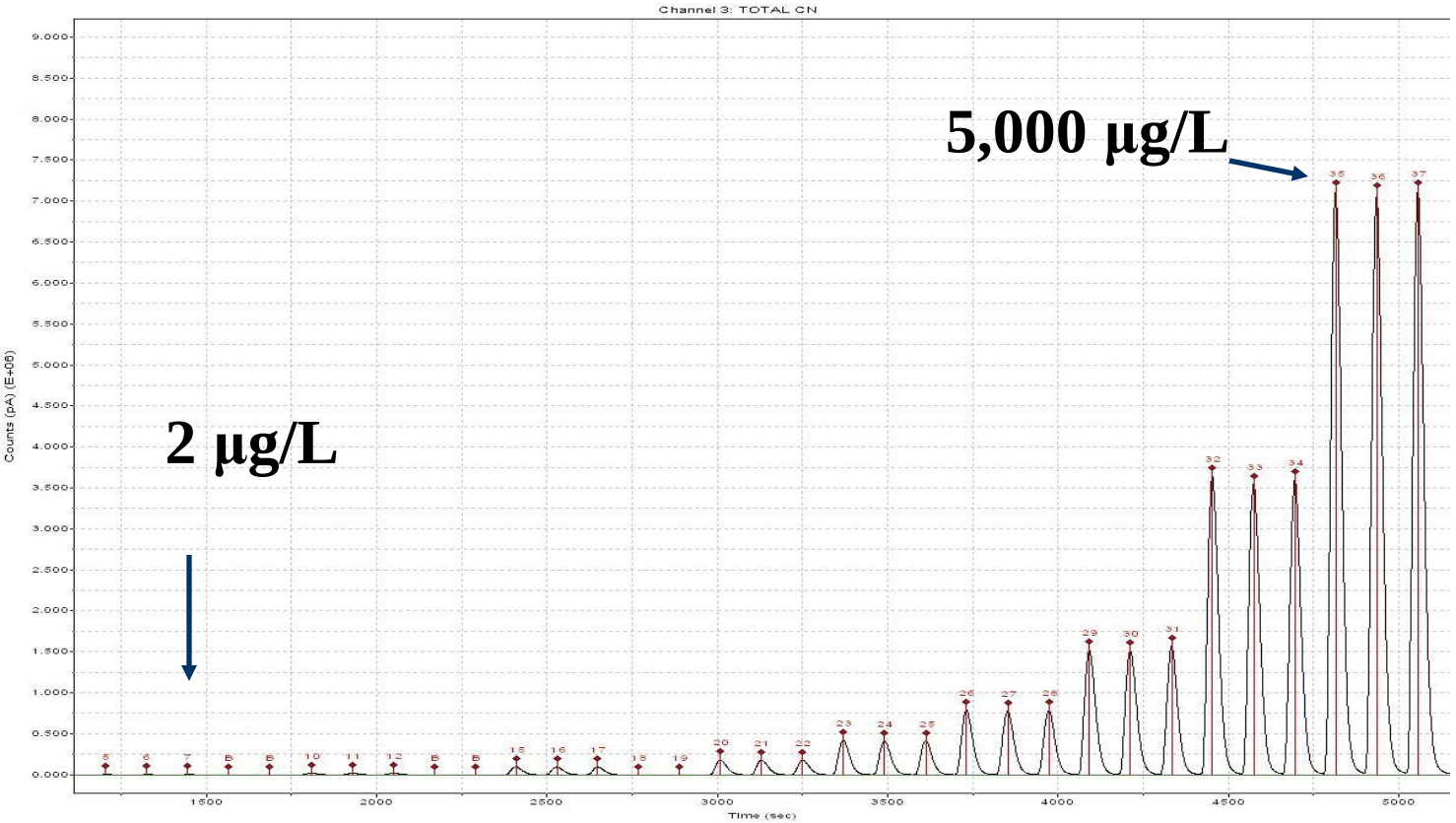


O·I·Analytical

Total Cyanide without Distillation

- Simplified method that does not suffer from the many interferences introduced by distillation.
- Cyanide complexes release cyanide after UV irradiation.
- The Hydrogen Cyanide formed diffuses into a dilute NaOH stream.
- Cyanide is determined amperometrically.

Total Cyanide without Distillation



O·I·Analytical

Total Cyanide without Distillation

Species	Distillation Method 335.2 (% Recovery)	UV-Irradiation (% Recovery)
$[Zn(CN)_4]^{2-}$	99.5	97.2
$[Cd(CN)_4]^{2-}$	104	104
$[Cu(CN)_4]^{3-}$	97.7	100
$[Ag(CN)_2]^{-}$	97.8	104
$[Ni(CN)_4]^{2-}$	104	98.3
$[Hg(CN)_4]^{2-}$	95.8	96.7
$Hg(CN)_2$	98.0	96.1
$[Fe(CN)_6]^{4-}$	101	102
$[Fe(CN)_6]^{3-}$	104	95.4
$[Pd(CN)_4]^{2-}$	69.1	17.7
$[Pt(CN)_4]^{2-}$	0.0	0.54
$[Pt(CN)_6]^{2-}$	0.0	0.0
$[Ru(CN)_6]^{4-}$	50.1	50.1
$[Au(CN)_2]^{-}$	56.6	49.5
$[Co(CN)_6]^{3-}$	0.0	13.8

O·I·Analytical

Eliminating Interferences

Interfering Species Added at 20 mg/L	Untreated Samples Method 335.2	Untreated Samples UV Irradiation	Treated Samples Method 335.2	Treated Samples UV Irradiation
Nitrite	0.155	0.199	0.203	0.198
Sulfite	0.080	0.199	No treatment	No treatment
Chlorine	Not Detected	Not Detected	0.120	0.118
Thiosulfate	0.124	0.196	No treatment	No treatment
Thiocyanate	0.174	0.208	No treatment	No treatment
Sulfide	Not tested	0.198	0.120	0.189

* Cyanide added at 0.200 mg/L (EPA MCL SDWA)

O·I·Analytical

Interferences – UV Irradiation Method

- Thiocyanate can photo decompose to form CN^- and S^{-2}, which are positive interferences.
- S^{-2} can be complexed after formation, eliminating its interference.
- Thiocyanate interference is minimized by UV irradiation >312 nm.
- High amounts of surfactants can “poison” the gas diffusion membrane.

Total Cyanide without Distillation

- A simplified method that does not suffer from as many interferences as currently approved methods.
- Less than 1 mL of sample is required.
- Very little hazardous waste is generated.
- No pyridine-containing reagents.
- Amperometric detection is simple, very sensitive, selective, and has a large linear range.

References

- Zheng A., Dzombak D.A., Luthy R.G. *Effects of Thiocyanate on the Formation of Free Cyanide during Chlorination and Ultraviolet Disinfection of Publicly Owned Treatment Works Secondary Effluent*, Water Environment Research. Volume 76, Number 3, pp 205–212.
- Berman R., Christmann D., Renn C, A*utomated determination of Weak Acid Dissociable and Total Cyanide without Thiocyanate Interference* American Environmental Laboratory, June 1993.
- OIA Draft Method 1678
- OIA Method 1677

O·I·Analytical

Total Cyanide Without Distillation

William Lipps
OI Analytical
151 Graham Road
College Station TX 77845

O·I·Analytical
A World of Solutions