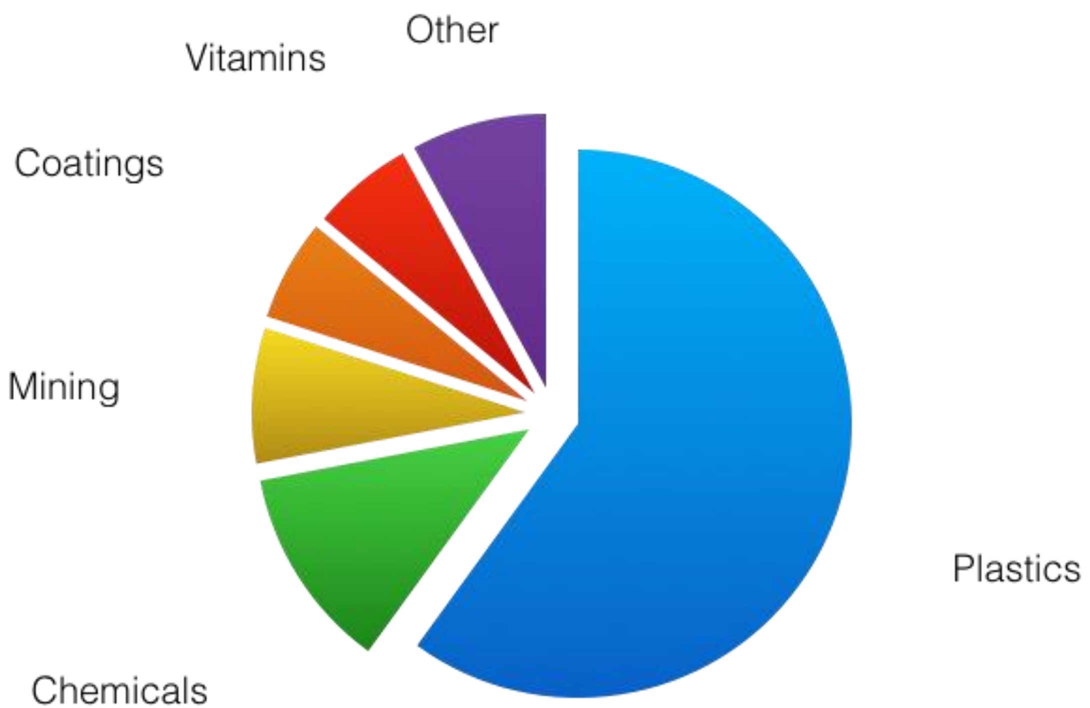
Cyanide Analysis:

Cyanide Chemistry, Methodology, Interferences, Sample Handling and Regulatory Updates

O·I·Analytical

Distribution of the Industrial Uses of CN

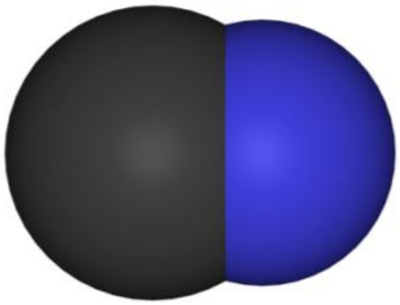


Who is measuring cyanide?

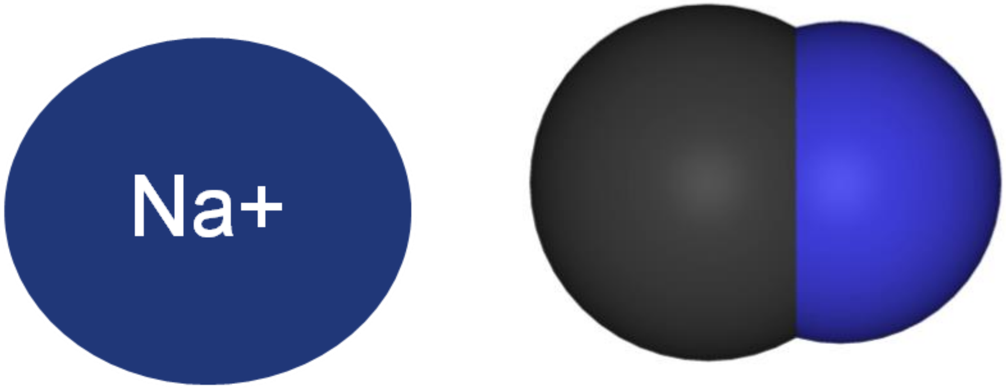
- NPDES
- Pretreatment
- SDWA
- Industrial hygiene
- Foods
- Beverages
- Mining
- Manufacturing

A generalized summary of cyanide and it's metal – cyanide species

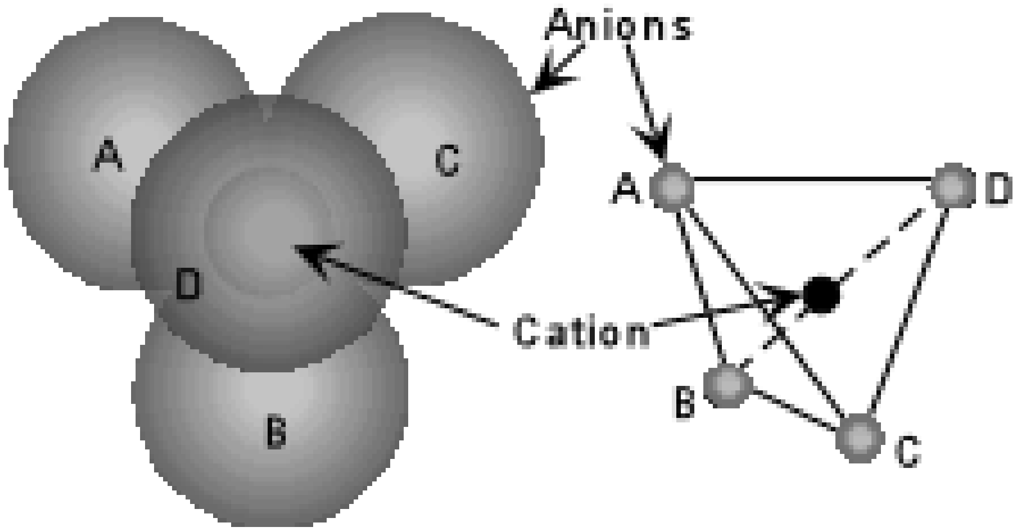
- Transition metals - strong bonds
- Alkali metals - ionic bonds



Free Cyanide is the CN ion and HCN, generate HCN at pH 6

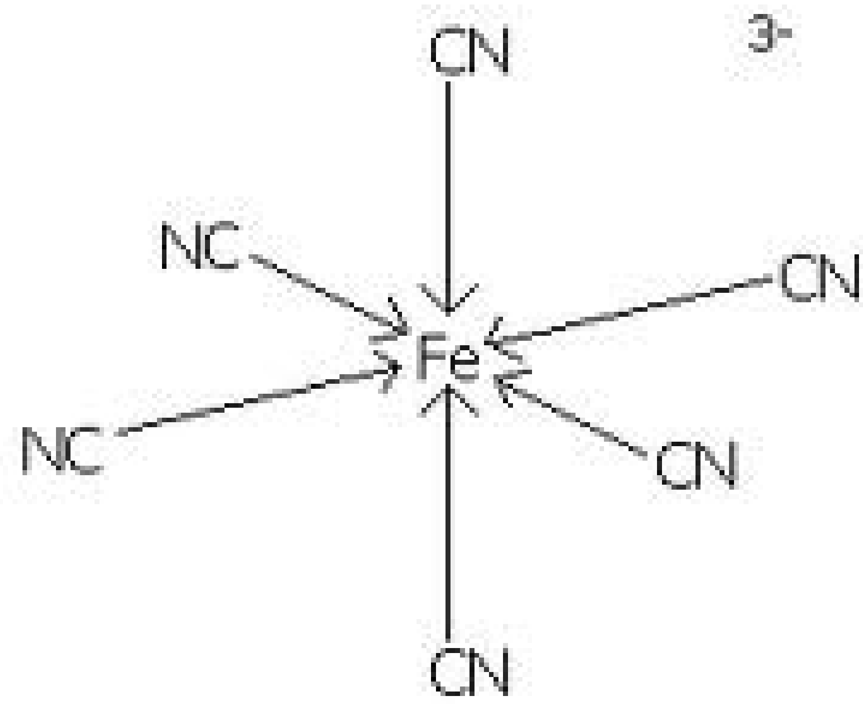


Metal Complexes require acid to generate HCN



Zn, Cd, Cu, Ni, Ag

Strong Metal Complexes are stable in acid solution

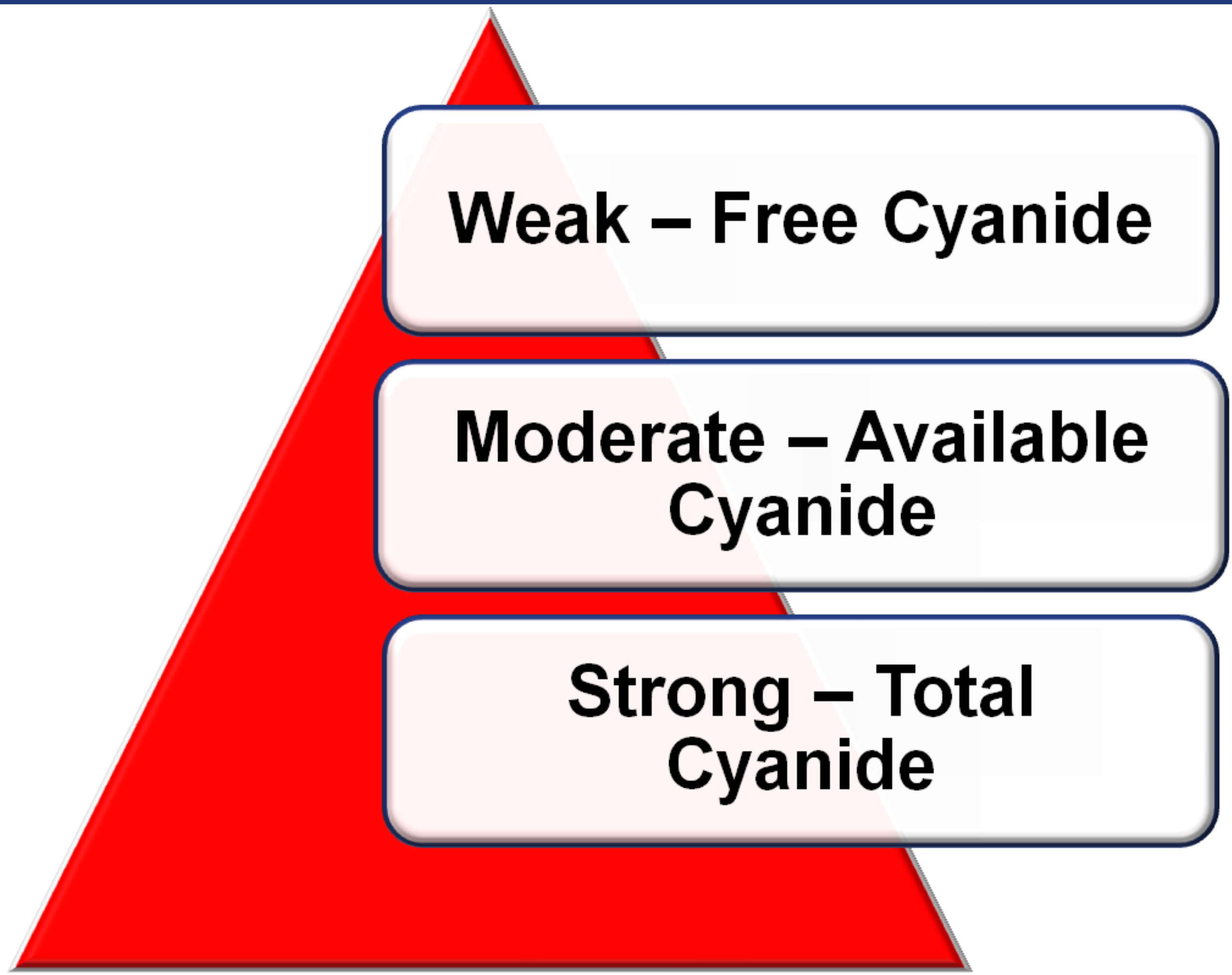


Iron Cyanide Complexes are very stable in the environment

$$[Fe(CN)_6]^{-3} + H^+ \longrightarrow 6\ HCN + Fe^{+3}$$

O·I·Analytical

Toxicity of Cyanide Complexes is related to its ability to produce HCN

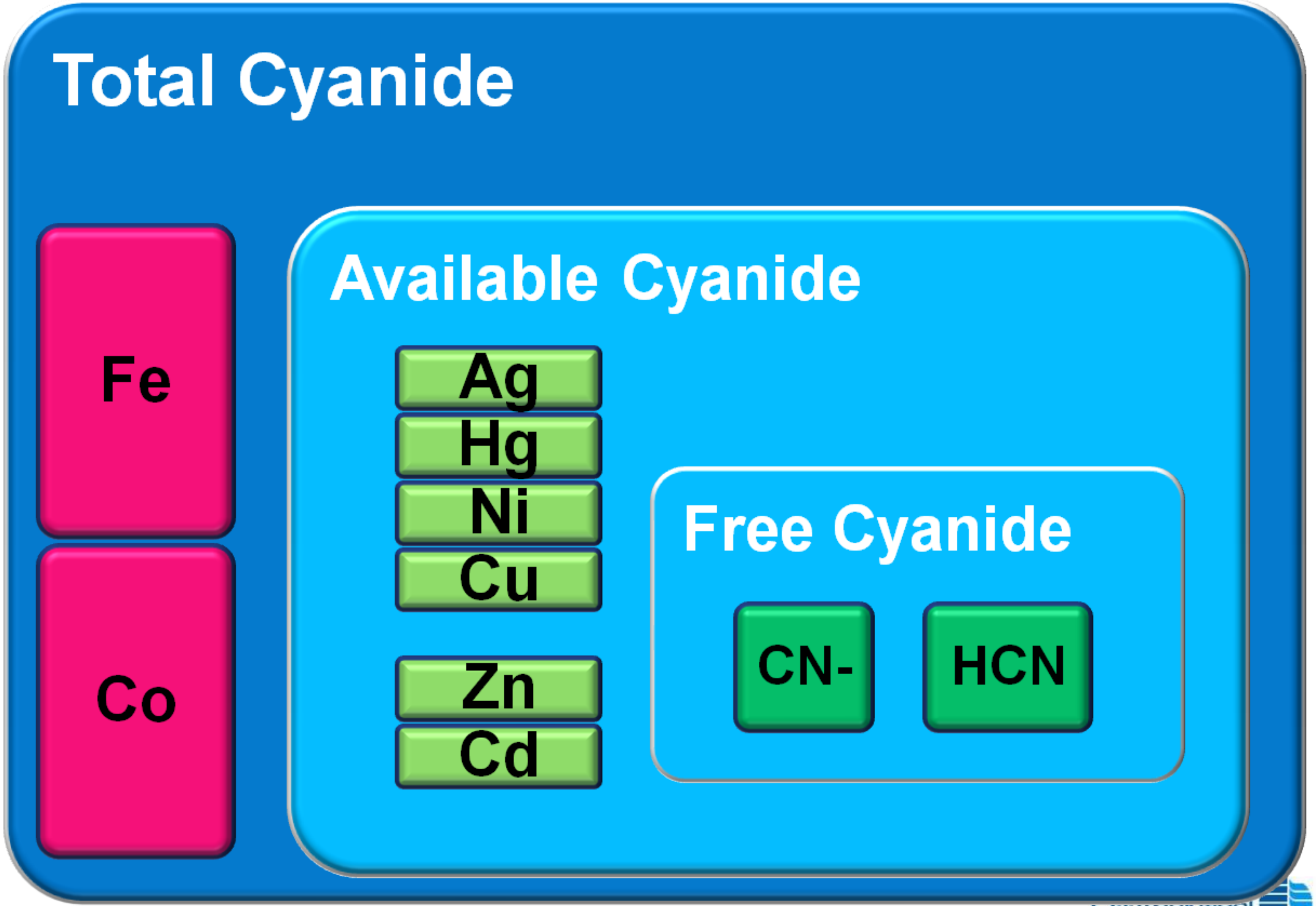


Cyanide methods measure the various cyanide "species"

- **Total CN**
  - Strong Metal Complexes
    - Fe, Co, Pt, Au
  - **Available CN**
    - Weak to Moderately Strong Metal Complexes
      - Ag, Cd, Cu, Hg, Ni, Zn
    - **Free CN**
      - HCN
      - CN^-

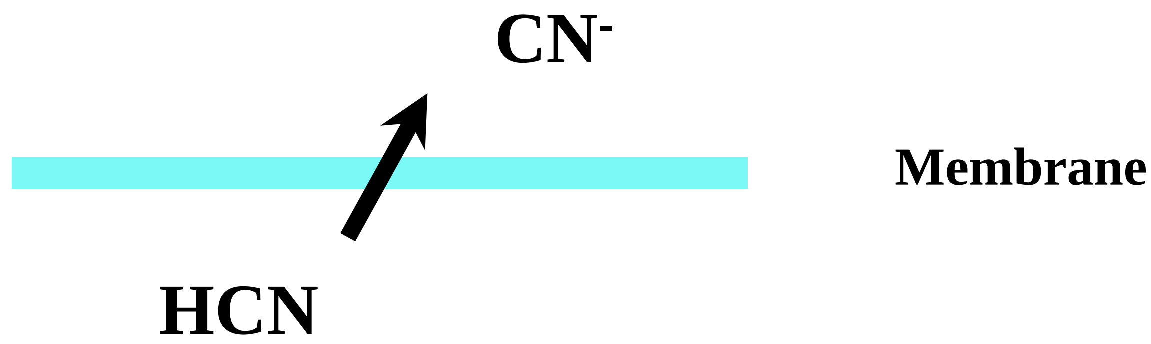
O·I·Analytical

Cyanide methods measure the various cyanide "species"



How Do You Measure Cyanide?

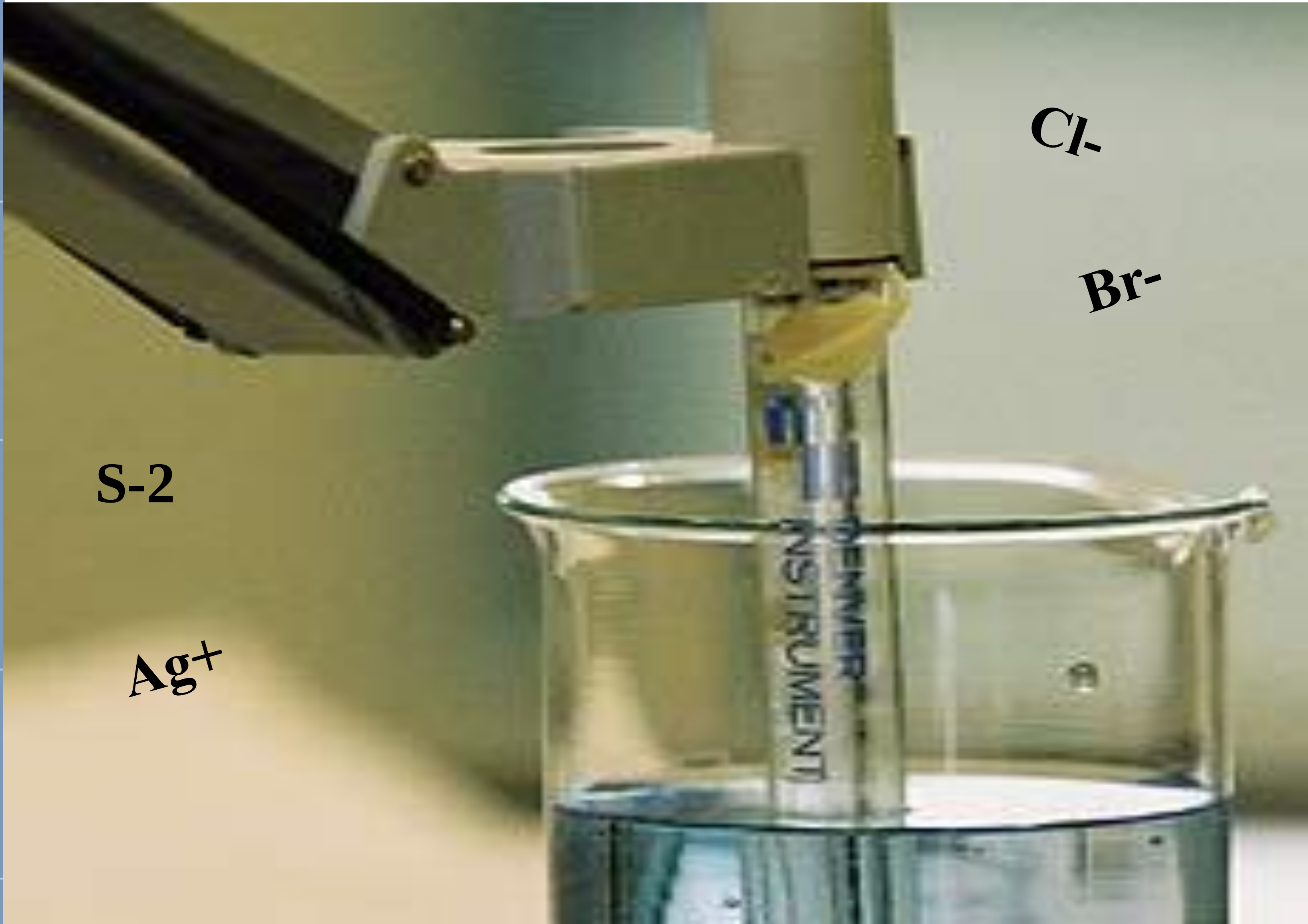
Gas diffusion - Amperometry



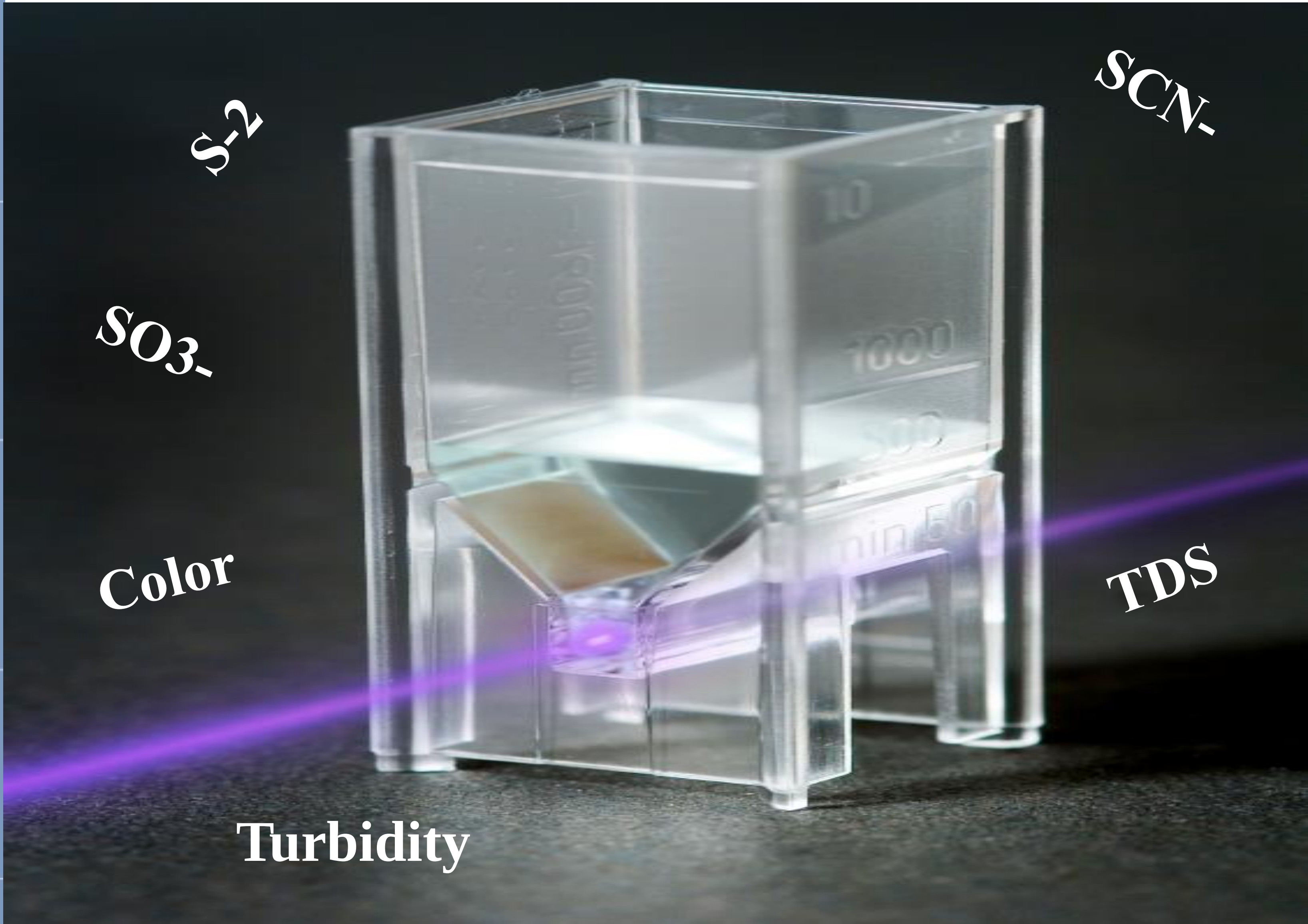
Sulfide > 50 ppm

Titration by silver ion

Ion Selective Electrode (ISE)



Colorimetric methods



Manual “distillation” is used to dissociate as HCN

Macro Distillation

MIDI Distillations

Distillation can be automated on a continuous flow analyzer

Distillation and condenser

Distillate

Cyanide Methods

Cyanide methods require separation of CN from matrix

- **Separated from interferences, cyanide measurement is no different than running standards.**

APPROVED METHODS

Free CN	GD-Amperometry	ASTM D7237
WAD CN	Distillation/ Colorimetry	ASTM D2036 or SM4500
CATC	Distillation/ Colorimetry	ASTM D2036 or SM4500
Available CN	GD-Amperometry	OIA 1677 or ASTM D6888

O·I·Analytical

Unlike colorimetry, GD amperometry is easy to visualize

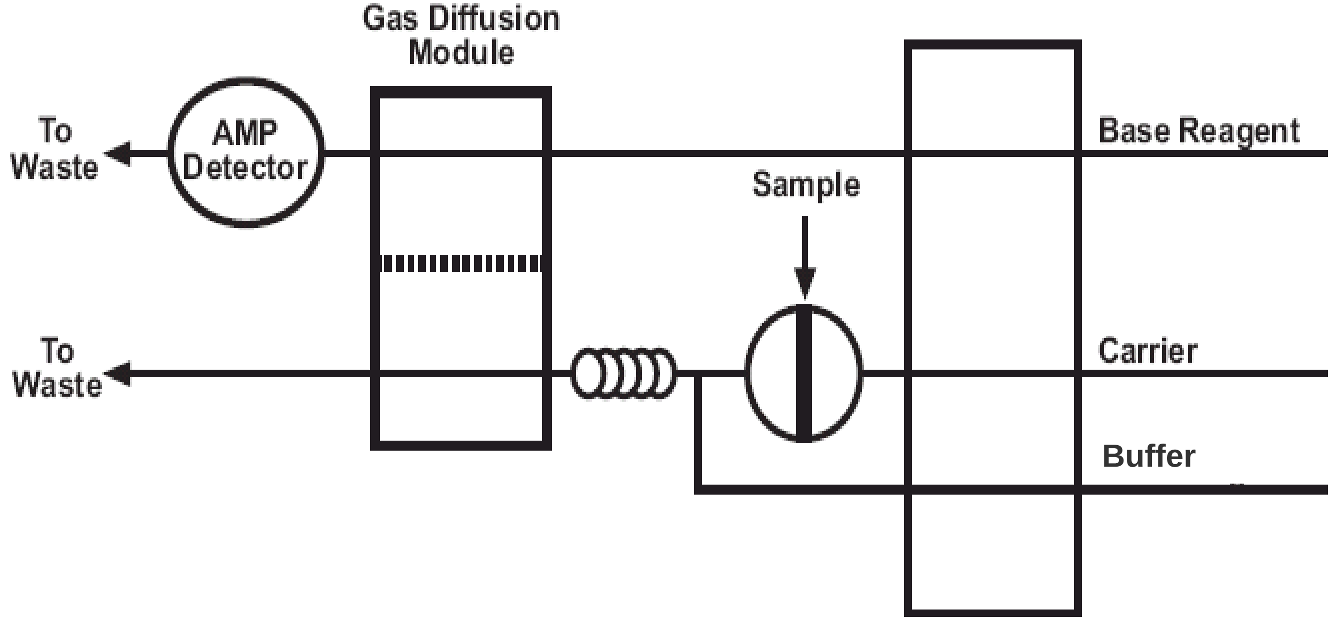
- $CN^- + H^+ \rightarrow HCN$
- $HCN + OH^- \rightarrow CN^- + H2O$
- $Ag + 2CN^- \rightarrow Ag(CN)_2^- + e^-$

measure

O·I·Analytical

Aquatic Free Cyanide Analysis

ASTM D7237-06 can be run on a OIA1677 CNSolution analyzer



Same Cartridge as OIA 1677

WAD Cyanide methods measure "available cyanide"

Method Number	Description	Measurement
SM 4500-CN I	Buffered pH 4.5 manual Distillation	Colorimetry
ASTM D 2036	Buffered pH 4.5 manual distillation	Colorimetry, Gas Diffusion - Amperometry

O·I·Analytical

Available Cyanide Analysis

WAD Cyanide methods measure “available cyanide”

Method Number	Description	Measurement
SM 4500-CN I	Buffered pH 4.5 manual Distillation	Colorimetry
ASTM D 2036	Buffered pH 4.5 manual distillation	Colorimetry, Gas Diffusion - Amperometry

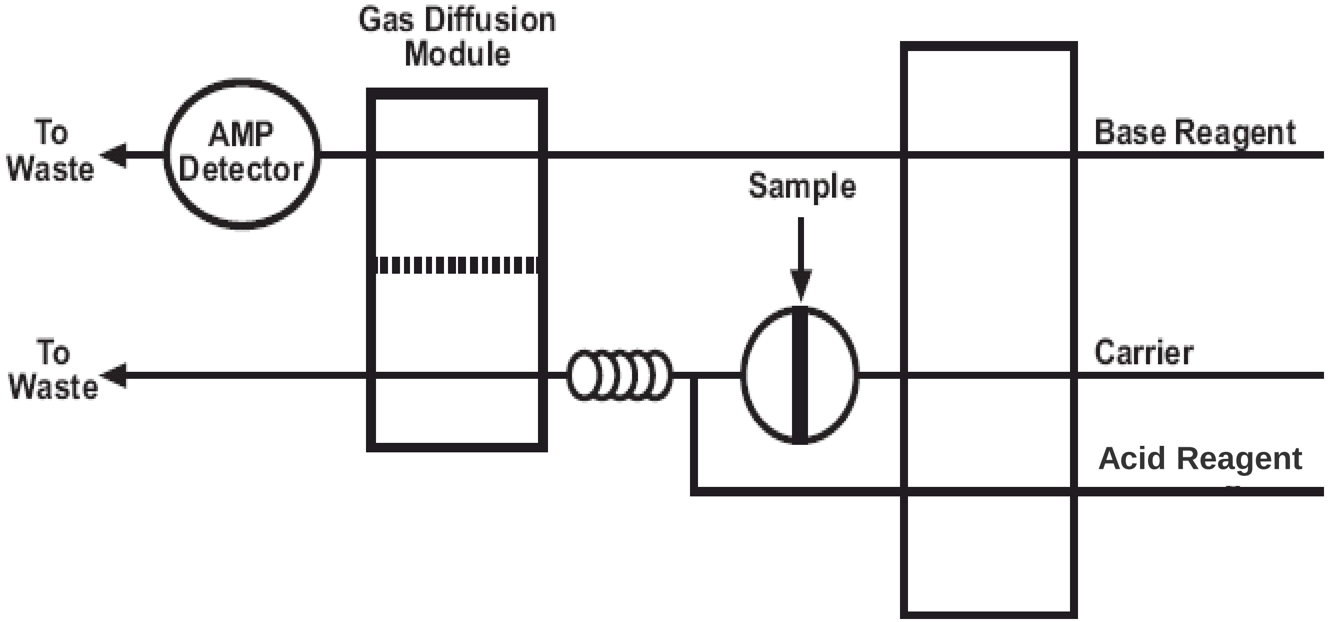
O·I·Analytical

Ligand Exchange methods measure available cyanide

Method Number	Description	Measurement
OIA 1677	Ligand Exchange / Flow Injection Analysis	Gas Diffusion - Amperometry
ASTM D 6888	Ligand Exchange / Flow Injection Analysis	Gas Diffusion - Amperometry

GD-amperometry methods do not require distillation

OIA 1677 or ASTM D6888 flow diagram



Ligand Exchange GD-amperometry methods have fewer interferences

CATC	WAD	OIA 1677
N-organics	Excessive Iron Cyanide	None
SCN, NH_3, NO_2	Concentration Dependent	—
S_2O_3, H_2O_2	—	—
Concentration Dependent	—	—

Ligand Exchange GD-amperometry methods provide the best benefits

- No distillation (eliminates 1 – 4 hours preliminary sample treatment)
- Low MDL (0.5 ppb)
- No Interferences
- High Throughput
  (up to 90 samples per hour)
- Ease of Operation, very simple chemistry.

Total Cyanide Methods

Automated gas diffusion distillation and non-distillation methods

Total Cyanide Methods – Manual Distillation

Method Number	Description	Measurement
SM 4500-CN C	Manual Macro Distillation – Mg Cl_2	Manual colorimetry / ISE
ASTM D 2036	Manual Macro Distillation – $MgCl_2$	Manual colorimetry, ISE, GD-amperometry, IC
EPA 335.4	Midi Distillation – $MgCl_2$	Automated Colorimetry
ASTM D 7284	Midi / Micro Distillation – $MgCl_2$	Gas Diffusion - Amperometry

O·I·Analytical

Automated total cyanide methods use UV to liberate HCN from Fe

Descriptive Name	Method Number	Description	Measurement
Total Cyanide	ASTM D4374 (Kelada 01)	High power UV-Auto distillation Alkaline pH	Automated colorimetry
	EPA 335.3	Low power UV-Auto distillation pH <2	Automated Colorimetry
	OIA 1678/ASTM D7511	Low power UV-pH <2	Gas Diffusion - Amperometry

O·I·Analytical

Comparison of Kelada and OIA 1678

	Kelada 01	ASTM D7511
Pump Tubes	15	5
Reagents	Pyridine	No Pyridine
Distillation	Yes	No
SCN Interaction	0.25 – 0.5 %	0.01 – 0.03 %

Comparison of Total CN methods

	335.4	ASTM D7284	ASTM D7511
Sample Preparation	2 – 3 hour distillation	1 – 3 hour distillation	No distillation
Analysis	1 – 2 minutes	1 – 2 minutes	1 – 2 minutes
Total Time	3 – 4 hours	2 – 4 hours	1 – 2 minutes

Advantages - CNSolution 3100

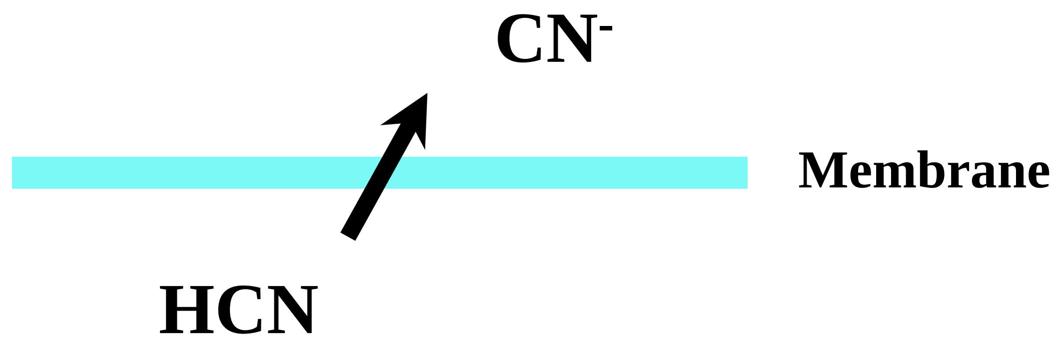
Total Cyanide	Distillation/ Colorimetry	EPA 335.4
	Distillation / GD-Amperometry	ASTM D7284
	No Distillation / GD-Amperometry	OIA 1678 (ASTM D7511-09)

One Instrument – multiple methods

O·I·Analytical

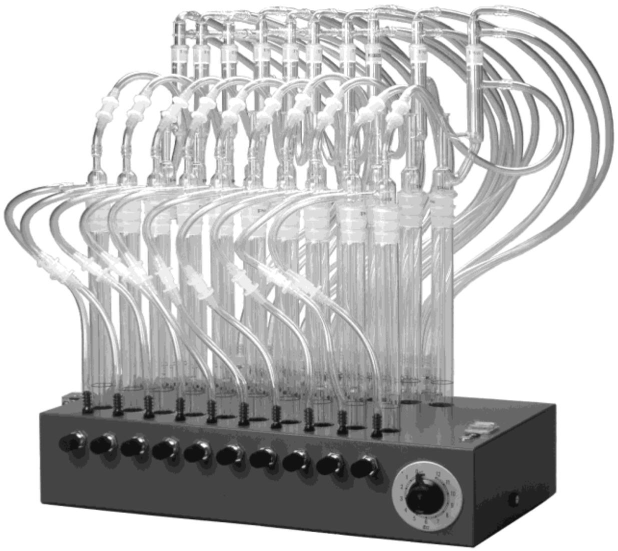
How do you solve interference problems caused by distillation?

Replace distillation with gas diffusion



Distillation most common technique to remove interference

Macro Distillation



MIDI
Distillations

Many cyanide interferences result from distillation

- Destroy CN
- Create CN

- UV distillation colorimetry - worst

Distillation actually creates CN interferences

- **Boiling acid**

- **Automated UV-Distillation**
  - **Boiling acid**

Interferences –

Thiocyanate

Destroy CN

Create CN

O·I·Analytical

Thiosulfate reacts with cyanide during distillation

- 0.200 mg/L CN^- + 200 mg/L $S_2O_3^{-2}$
  - Cyanide Found = 0.160 mg/L
  - Recovery = 80%*
  - * Double Chloramine T added, or recovery would be lower.

These compounds are in almost every sample and interfere significantly

Thiocyanate

Sulfur and Sulfide

Interferences

Sulfur (IV) oxides

Oxidizers

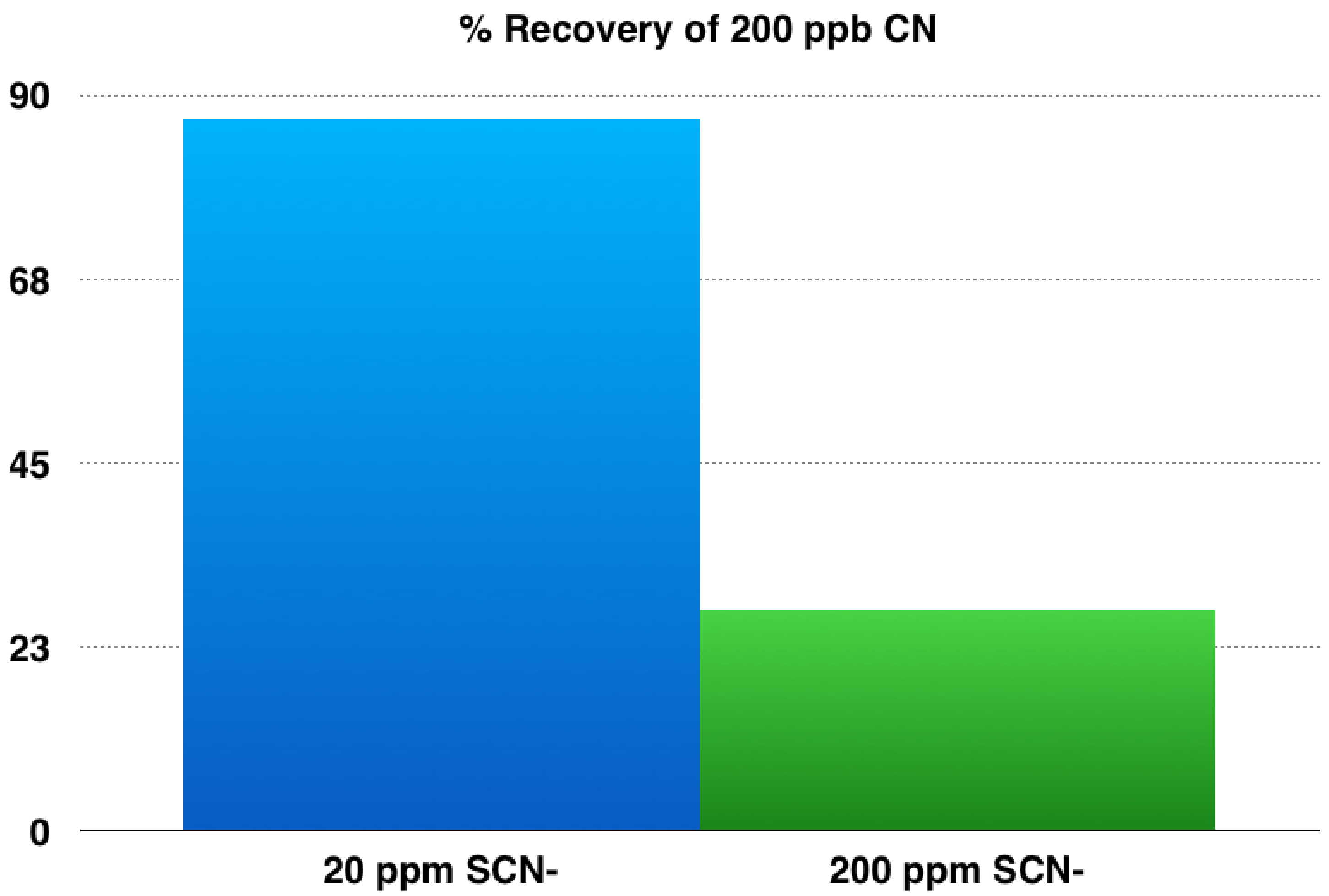
O·I·Analytical

Thiocyanate + Nitrate results in positive bias

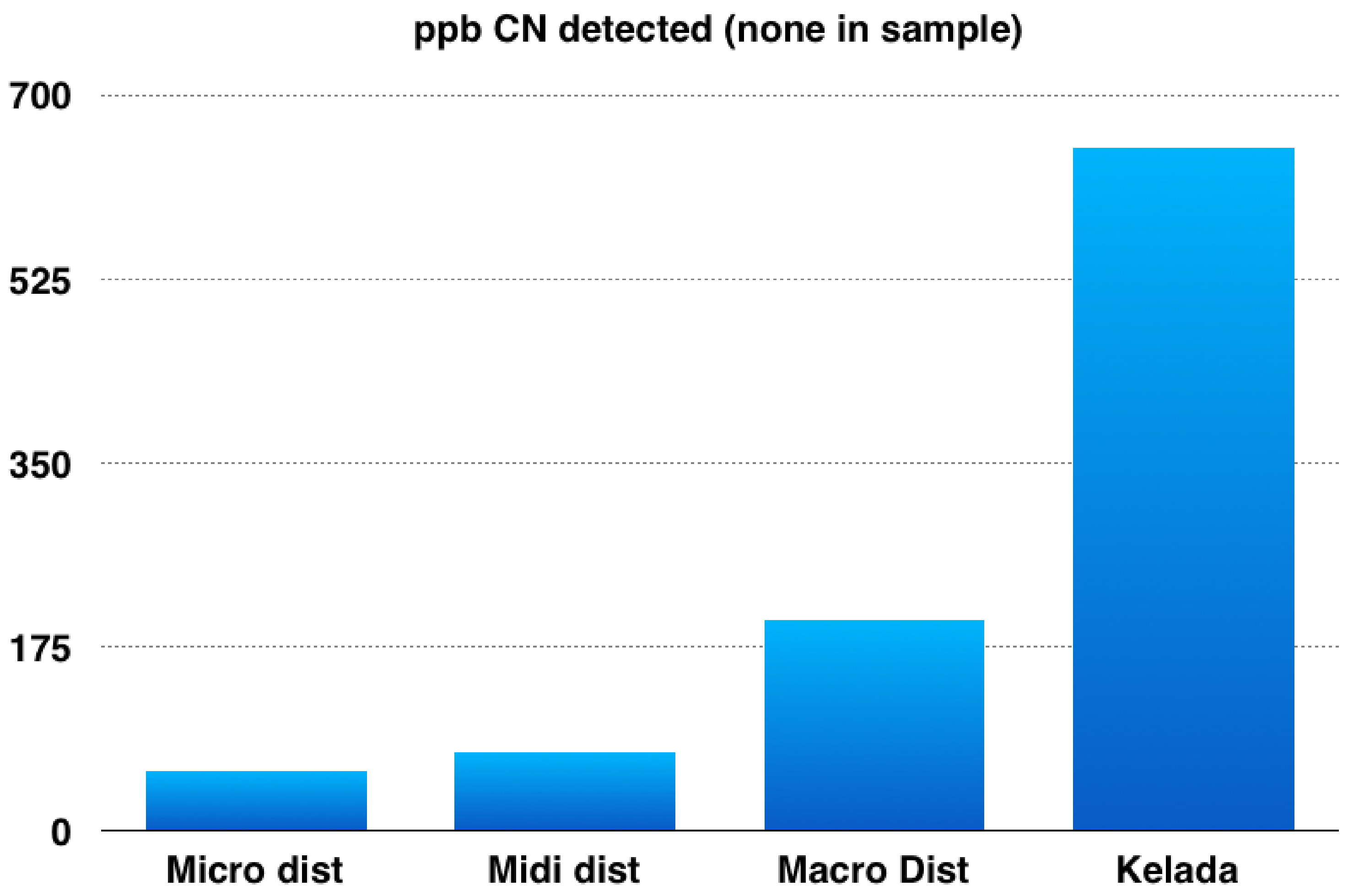
- **The addition of Sulfamic acid does not sufficiently reduce this interference.**
  - **A real POTW sample with 0.1 mg/L SCN^- and 63.5 mg/L NO_3^- detected total CN^- at 0.10 mg/L even after the addition of Sulfamic Acid**

O·I·Analytical

Interferences – Thiocyanate



Interferences – Thiocyanate and Nitrate

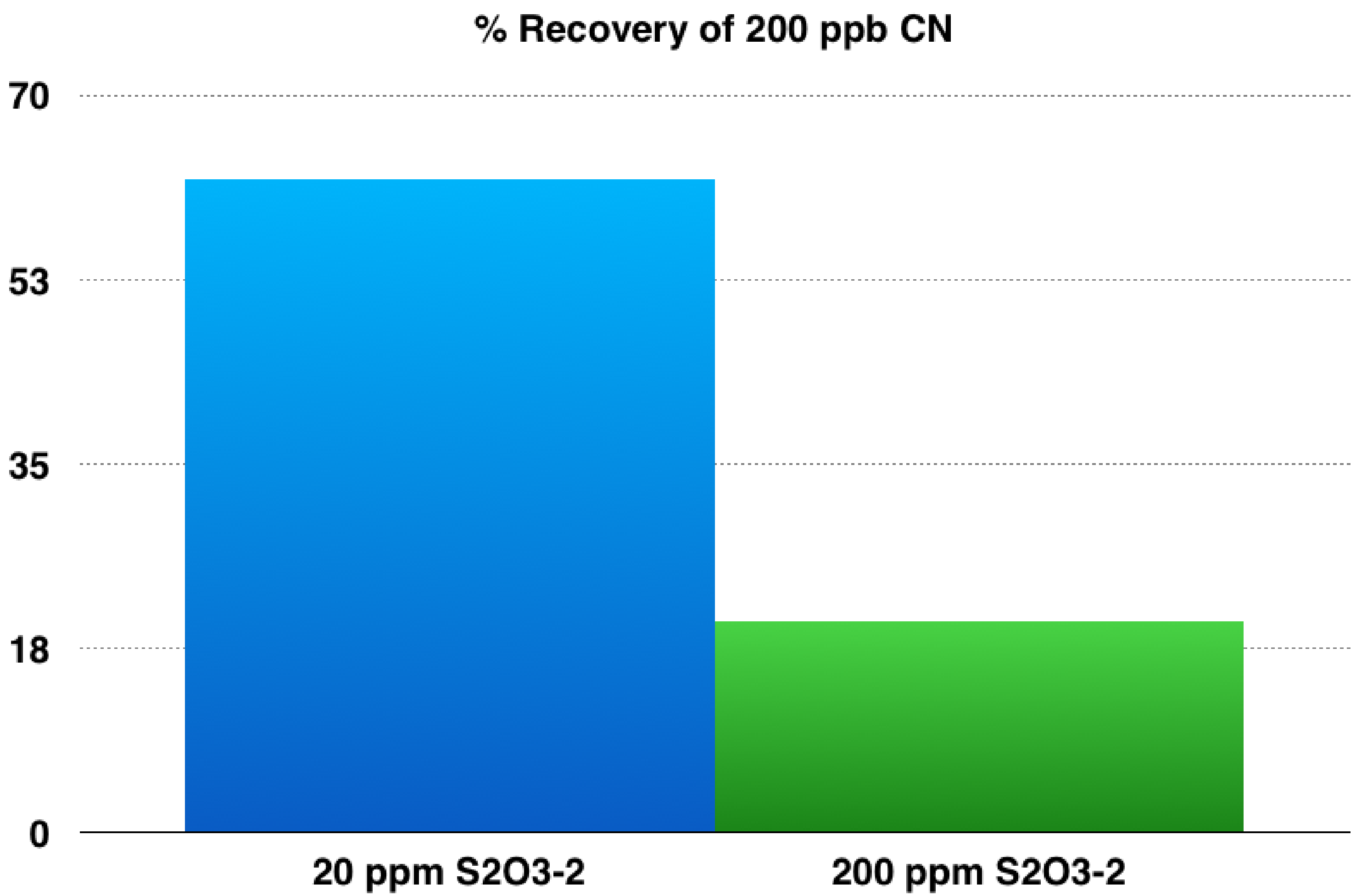


Sulfite reacts rapidly with CN in basic solutions

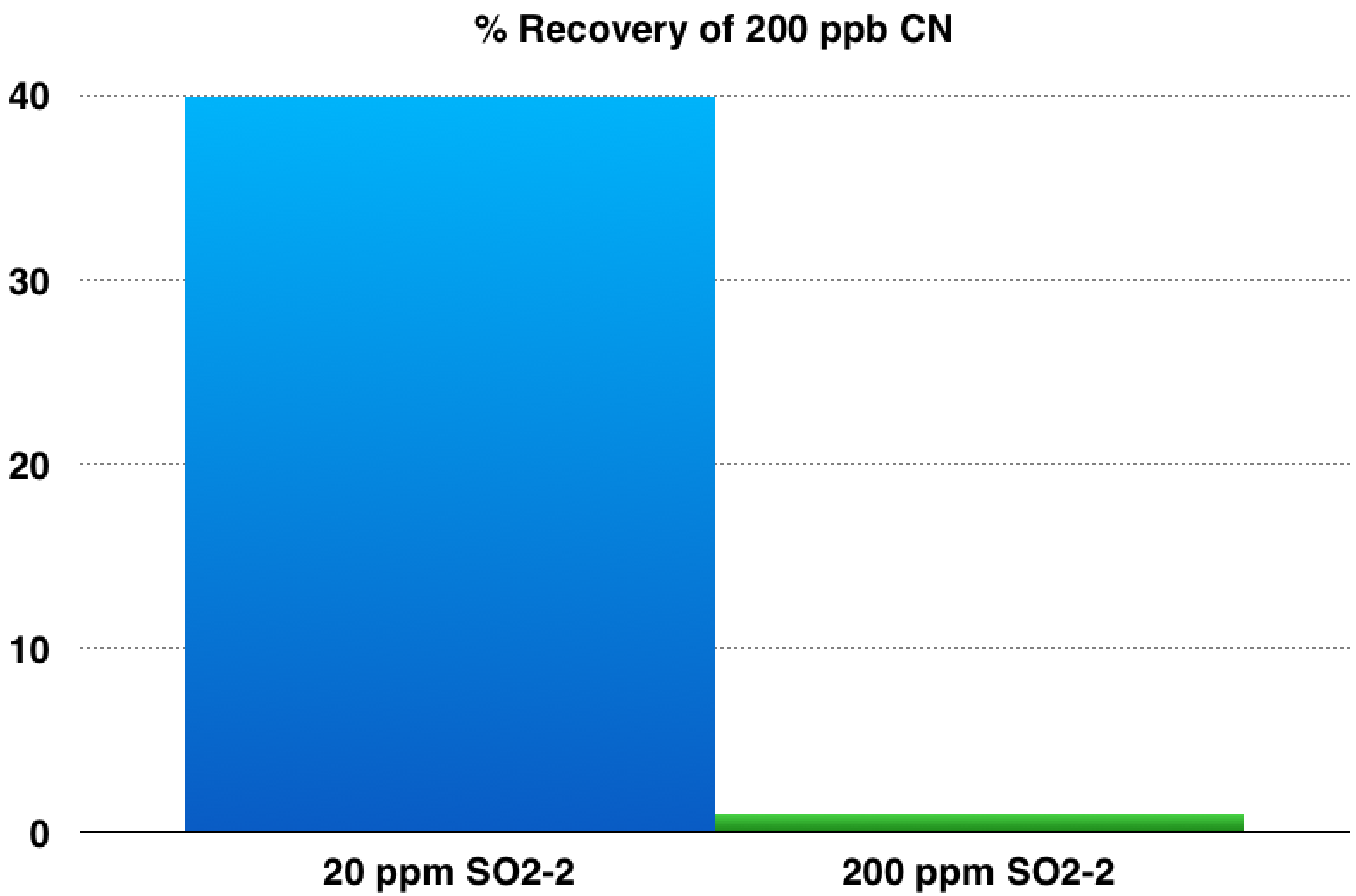
- **0.200 mg/L CN^- + 200 mg/L SO_3^{-2}**
  - **Cyanide Found = 0.000 mg/L**
  - **Recovery = 0%**

- **This reaction occurs in absorber solution, or in preserved sample**

Interferences – Thiosulfate



Interferences – Sulfite



Interferences – Sulfur Compounds

- No Spot Tests
- Dechlorination

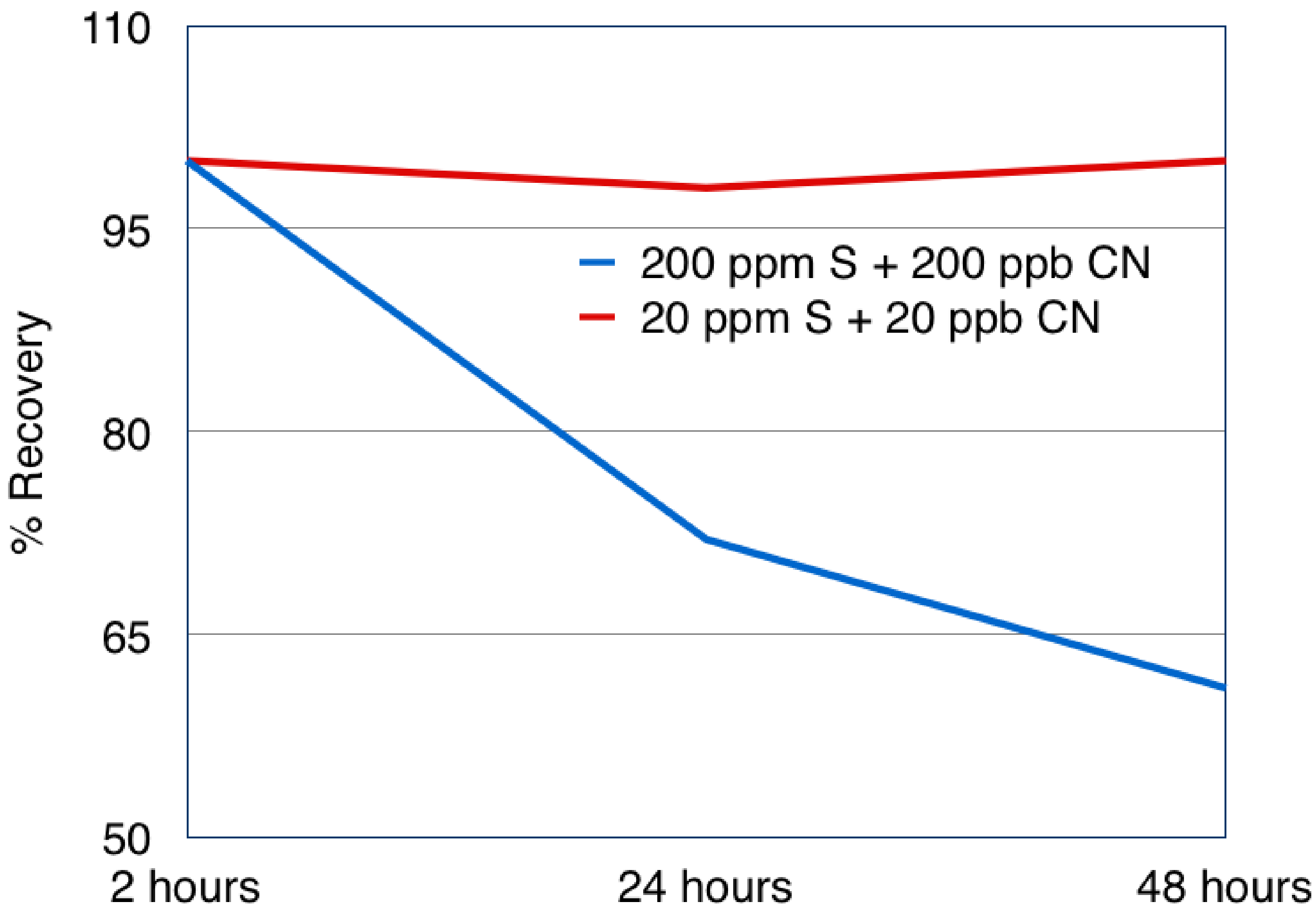
O·I·Analytical

Sulfur compounds react rapidly with CN

- Elemental Sulfur
  - $8CN^- + S_8 \rightarrow SCN^-$
- Metal Sulfides
  - Cu_2S, FeS, PbS, $CuFeS_2$, CdS, ZnS, etc.
  - S reacts with CN^- to form SCN^-

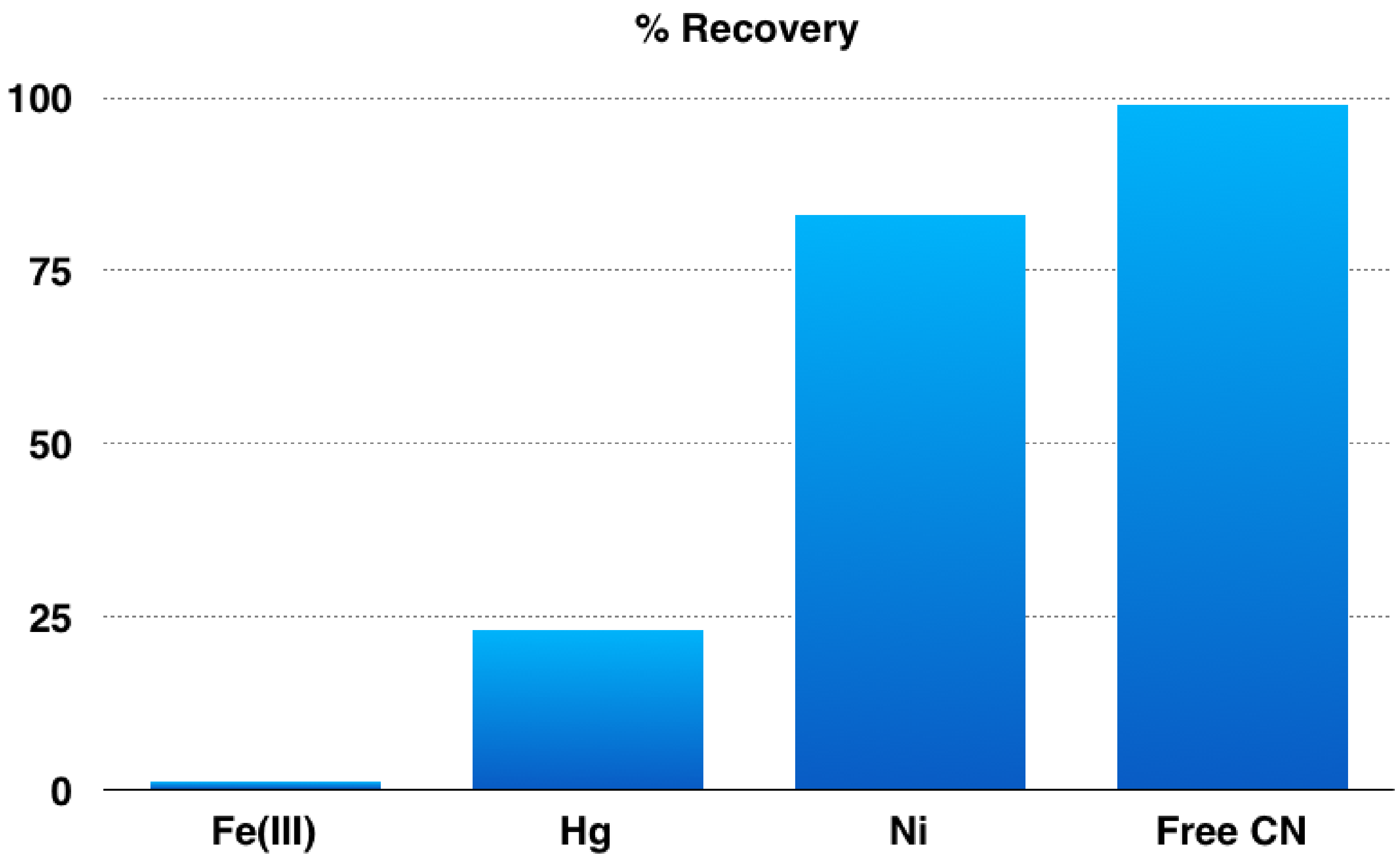
O·I·Analytical

Holding Time Study – Sulfide Bearing Samples

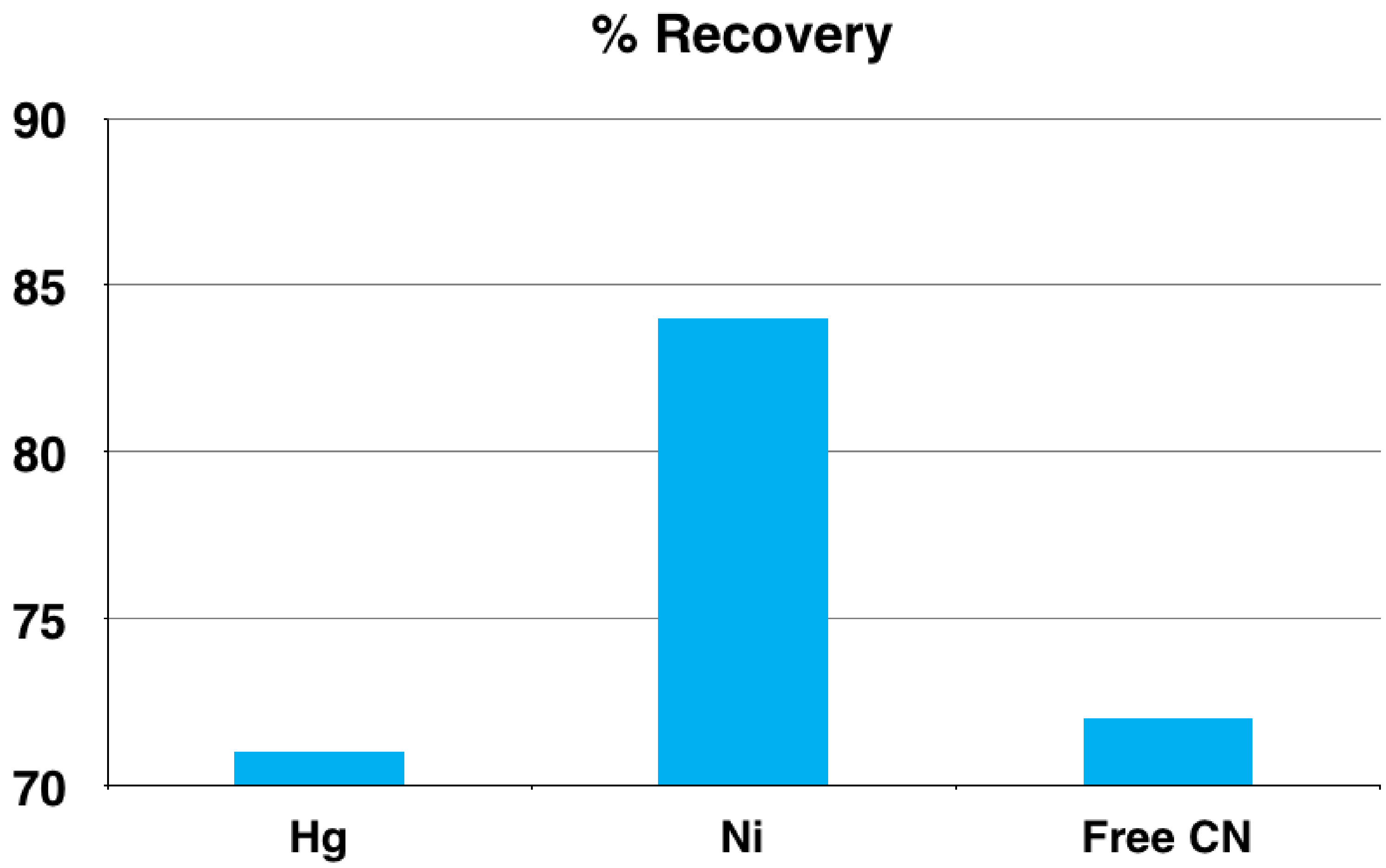


O·I·Analytical

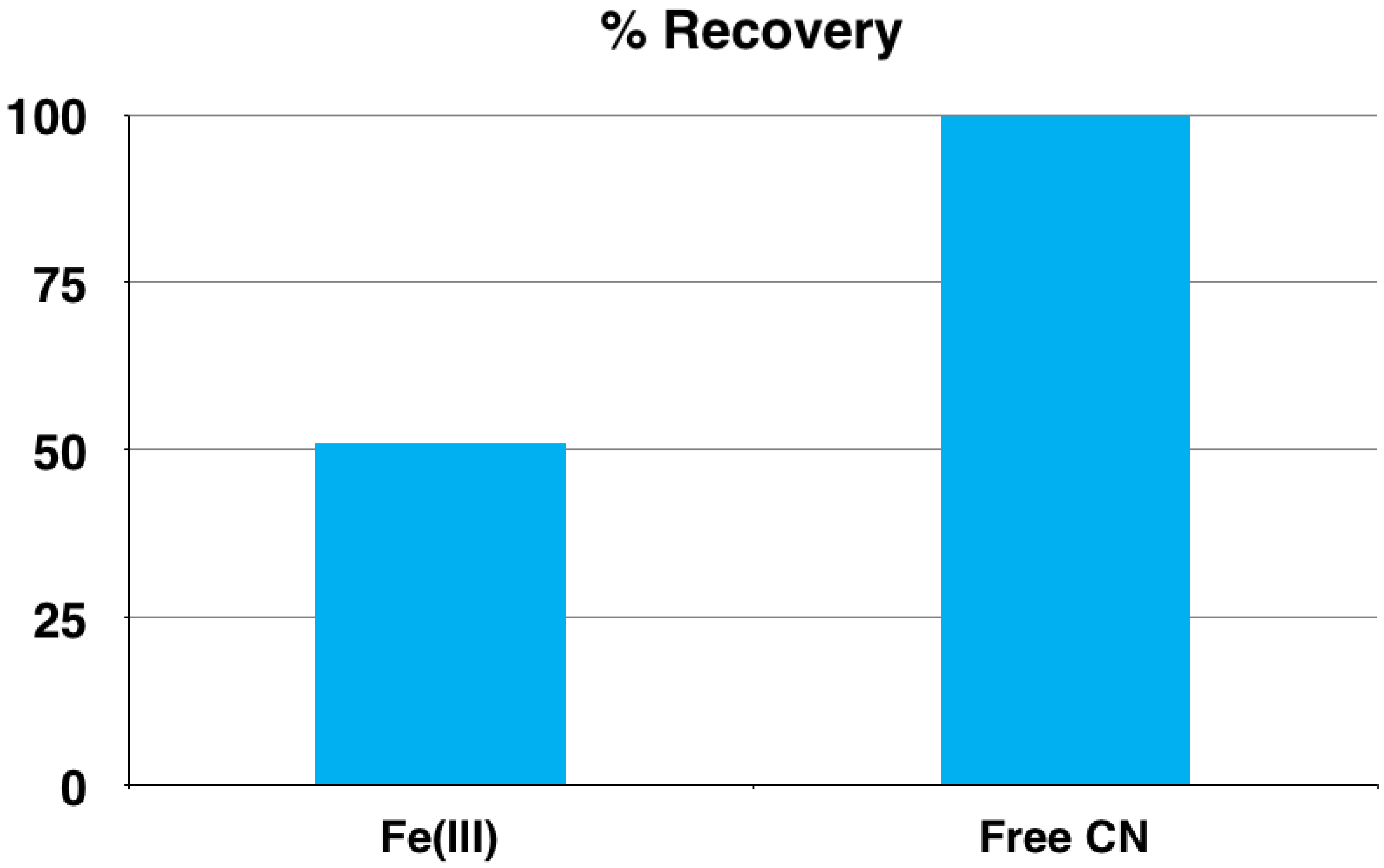
Cannot use Cadmium to Treat Sulfide



Headspace to Treat Sulfide



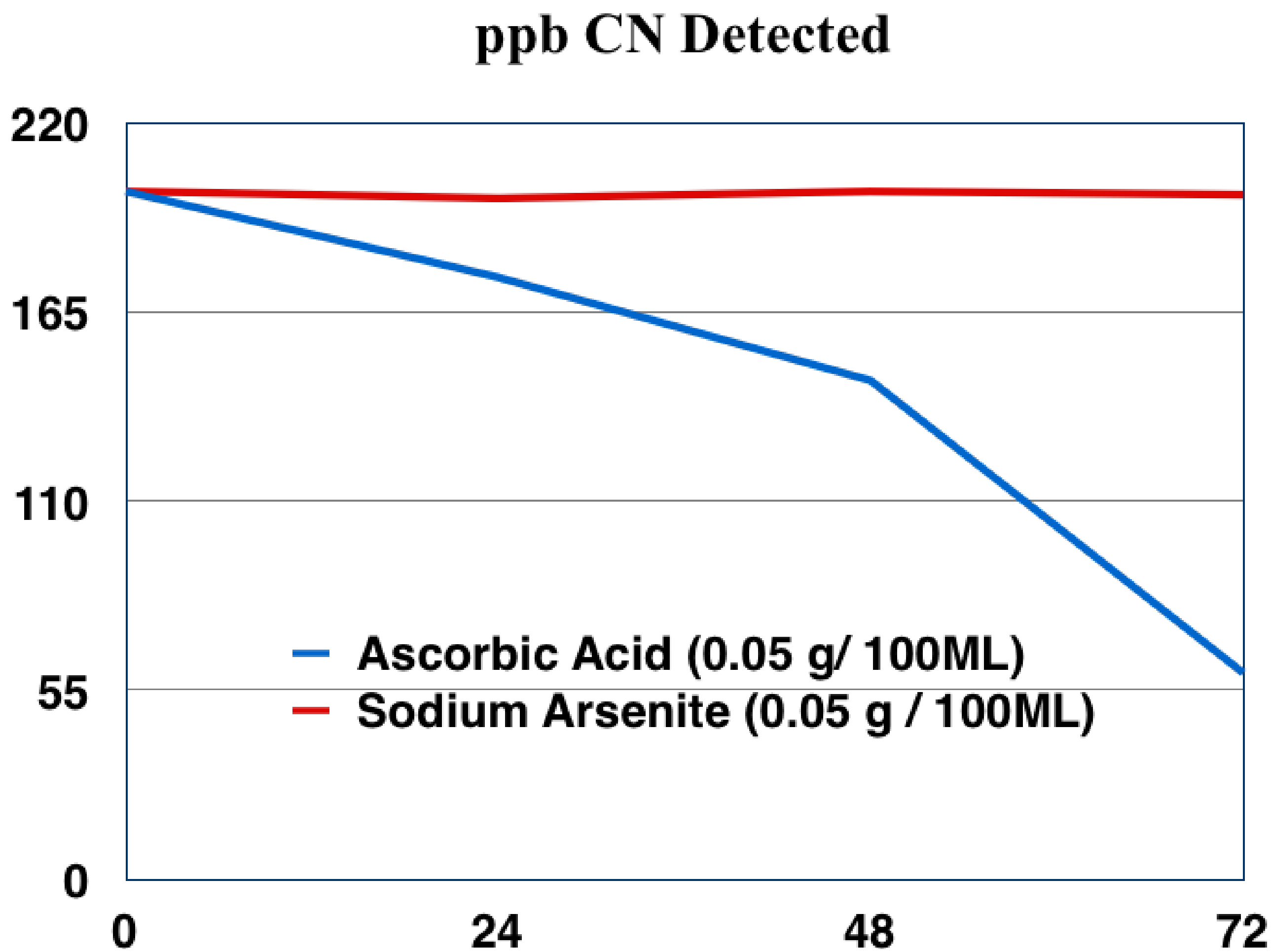
Bismuth to Treat Sulfide then distillation



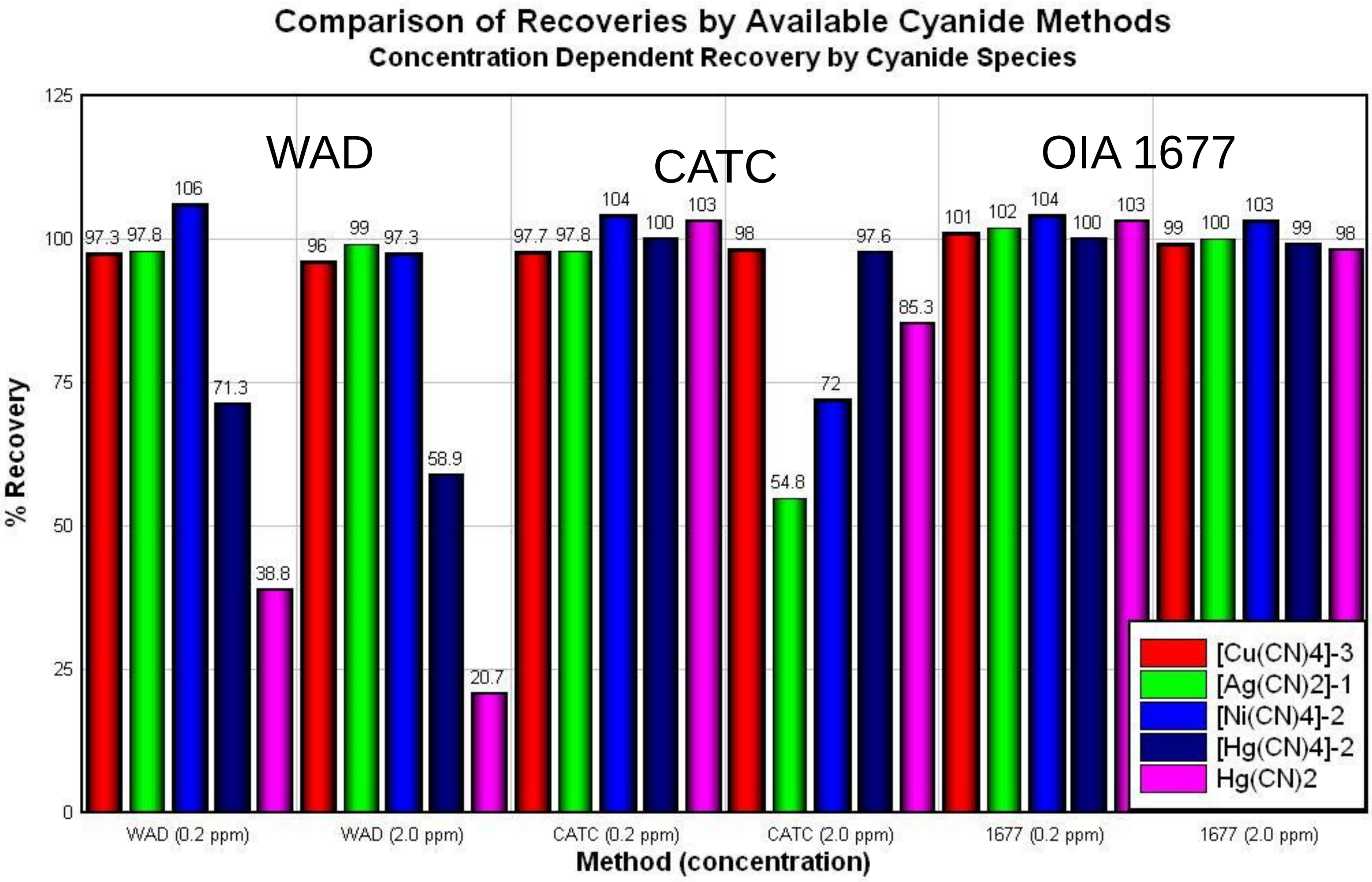
Oxidizers destroy cyanide before or during distillation

- Hypochlorite
- Peroxide
- Caro's Acid
- Chloramines

Oxidizer Removal



Ligand Exchange GD-amperometry methods get better recovery



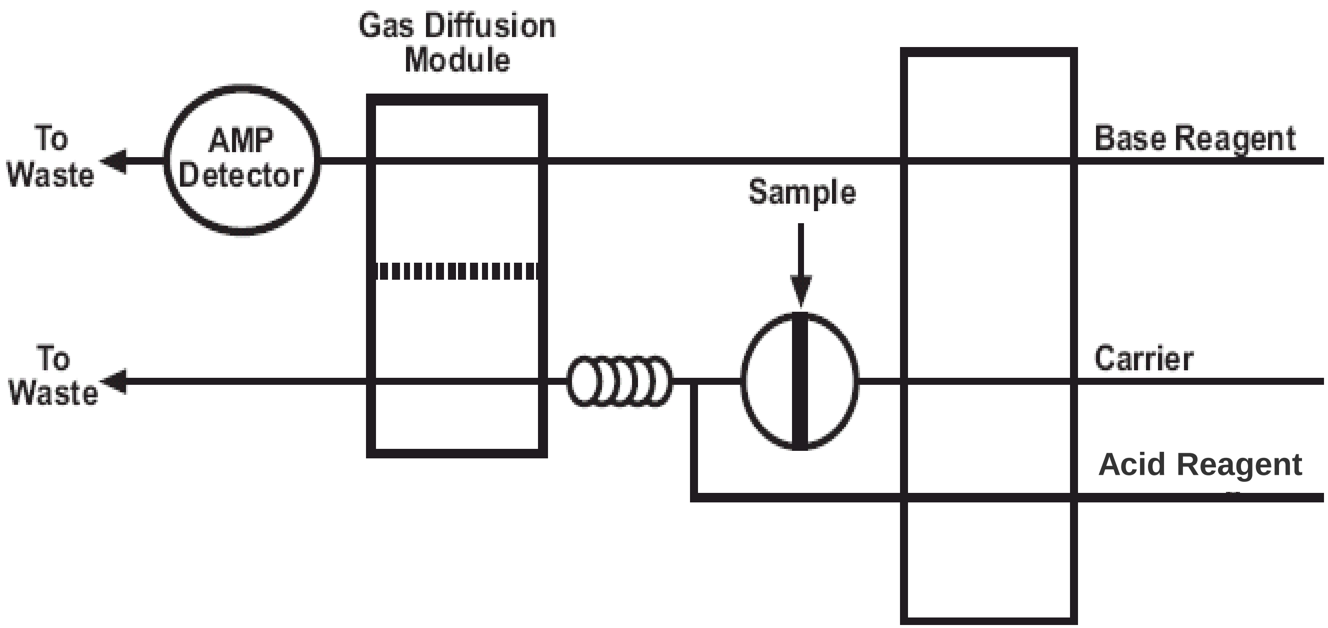
O·I·Analytical

Cyanide methods that utilize distillation have significant disadvantages

- **Time Consuming**
  - One hour long distillation (does not take into account setup and teardown)
  - CATC requires two, one hour distillations
- **Bulky and Relatively Expensive Glassware**
- **Operator-dependent results (technique)**
- **Multiple Interferences**

GD-amperometry provides the safest, easiest, and most accurate technique

No pyridine

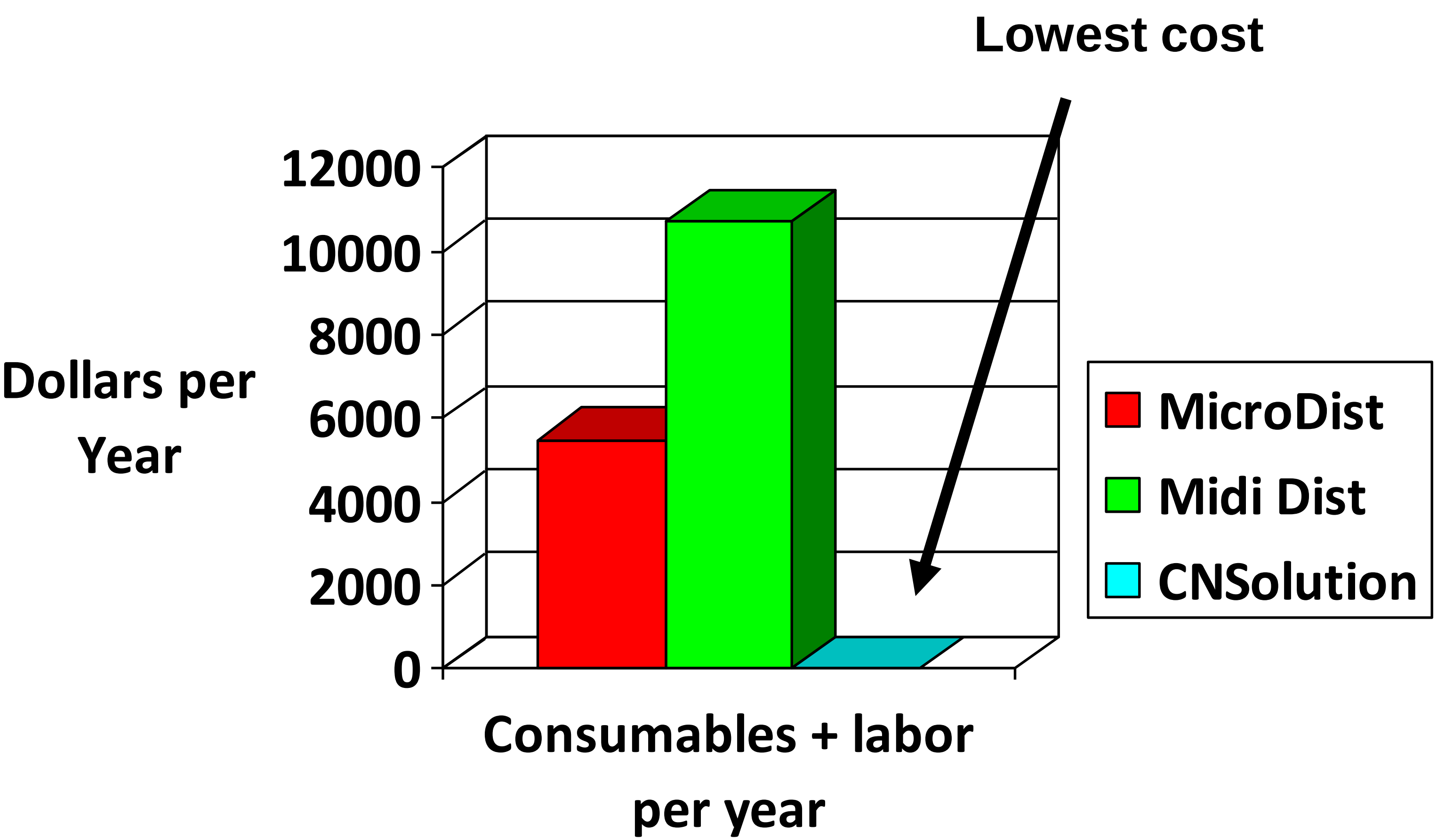


ASTM D7284-08 is a “green” chemistry

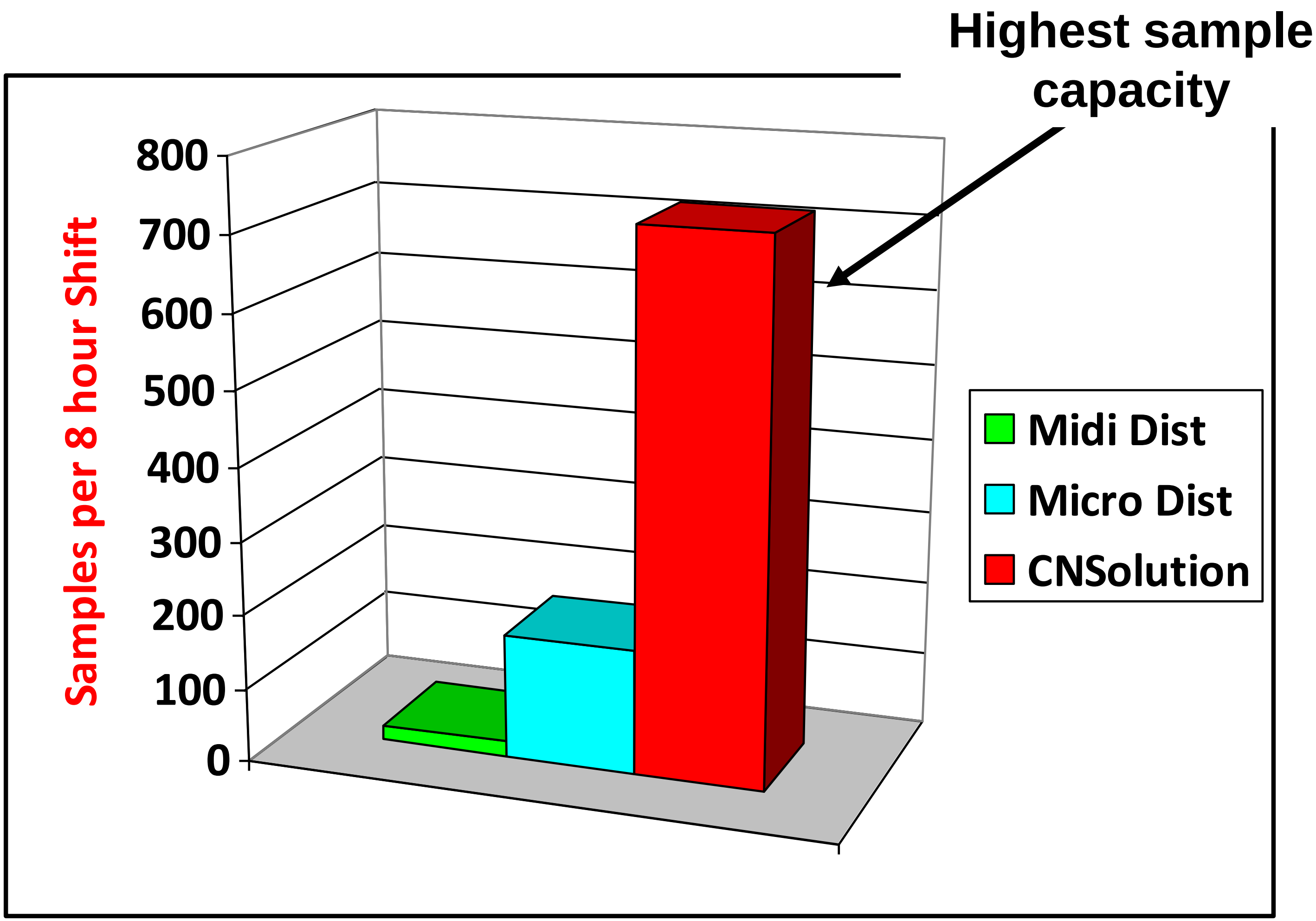
CNSolution 3100

- Rapidly Analyze Cyanide with Confidence in Results
  - Free Cyanide
  - Available Cyanide
  - Total Cyanide
- Eliminate Time Consuming, Error Causing Distillations
- Expand Capability to Colorimetric FIA and SFA

Gas diffusion eliminates distillation and associated cost



Eliminating distillation increases laboratory capacity

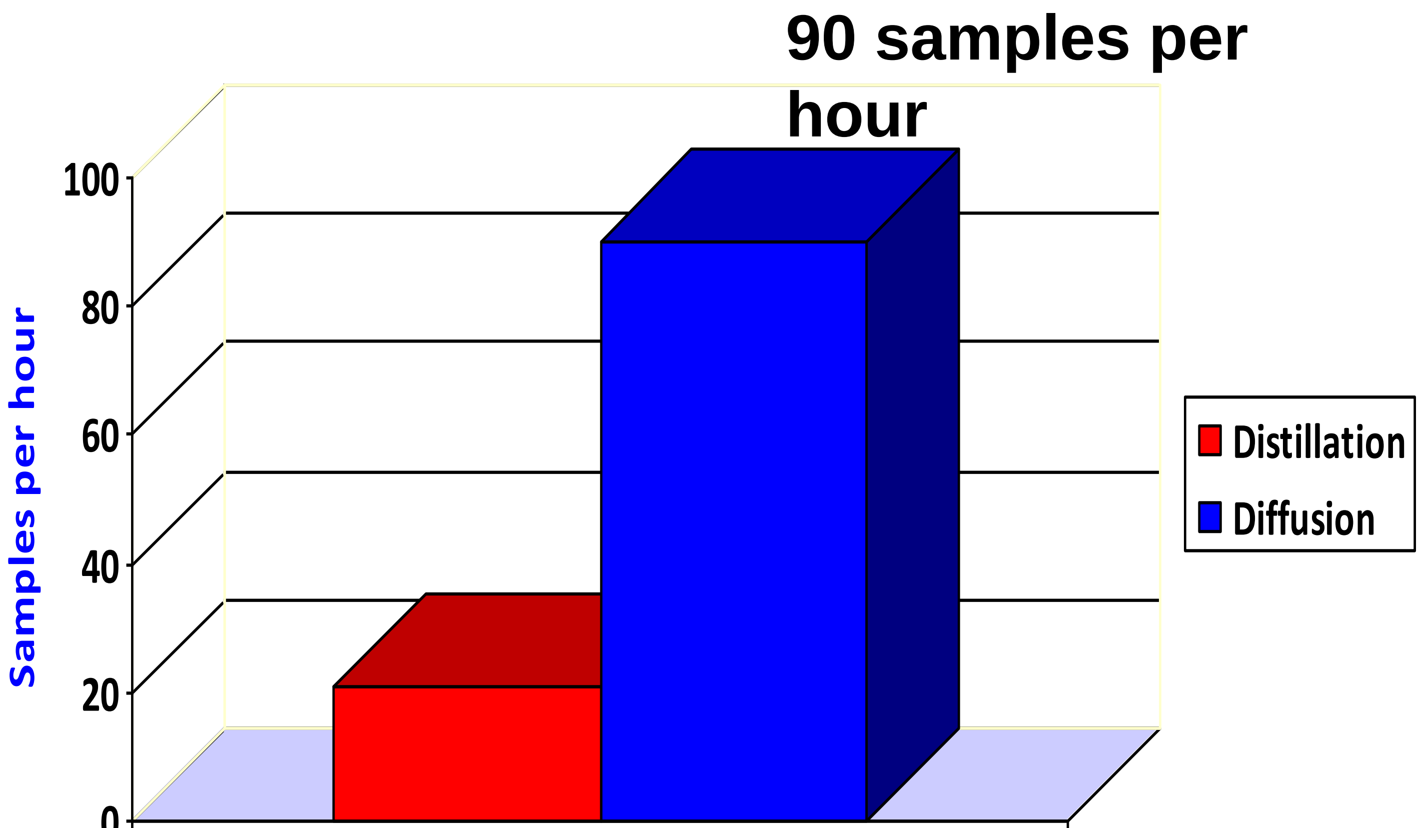


Ligand Exchange GD-amperometry methods give you results in minutes

	CATC	WAD	OIA 1677
Sample Preparation	2 distillations 2 – 3 hours	1 distillation 2 – 3 hours	No distillation
Analysis	1 – 2 minutes	1 – 2 minutes	1 – 2 minutes
Total Time	3 – 4 hours	3 – 4 hours	1 – 2 minutes

O·I·Analytical

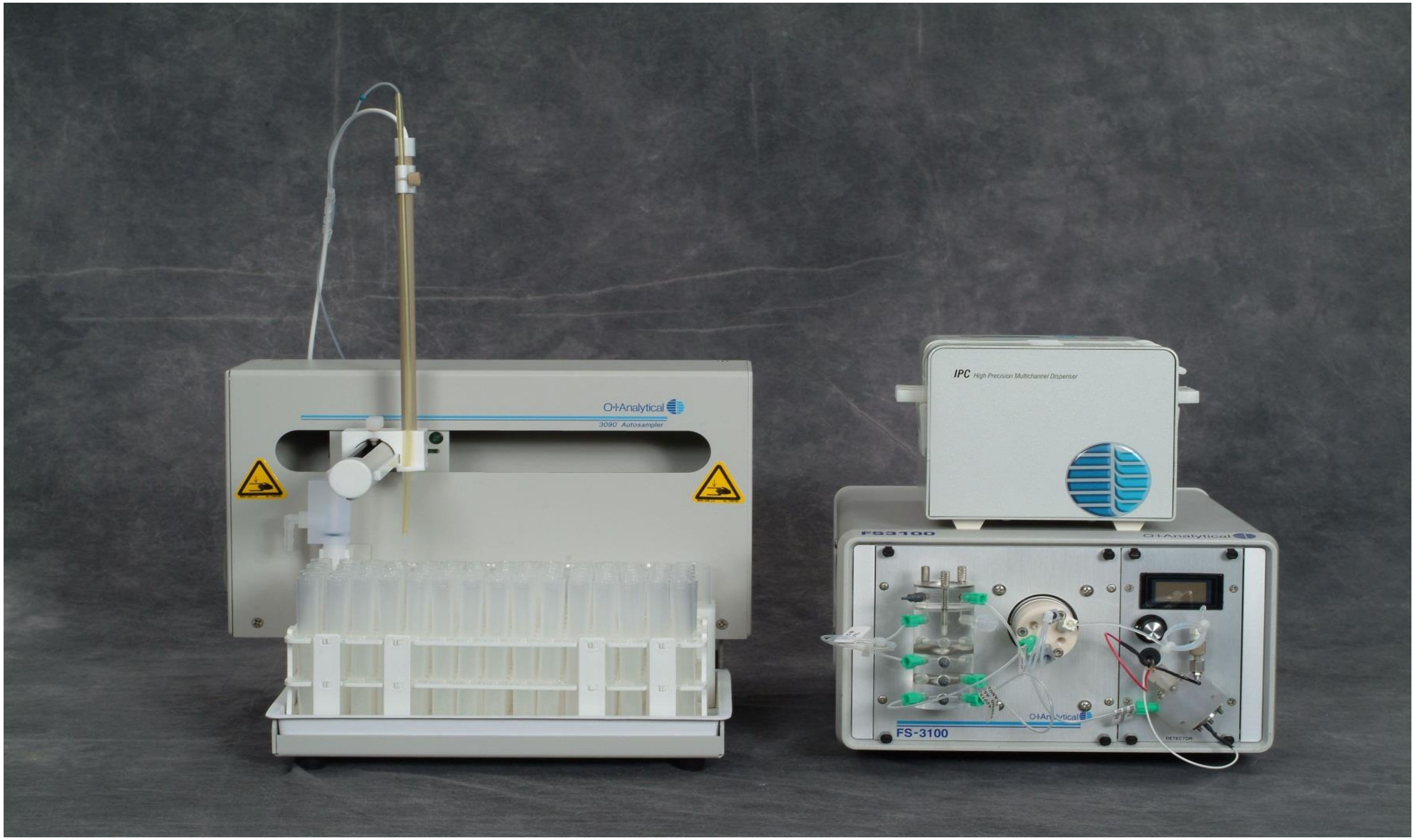
Ligand Exchange GD-amperometry methods means more samples



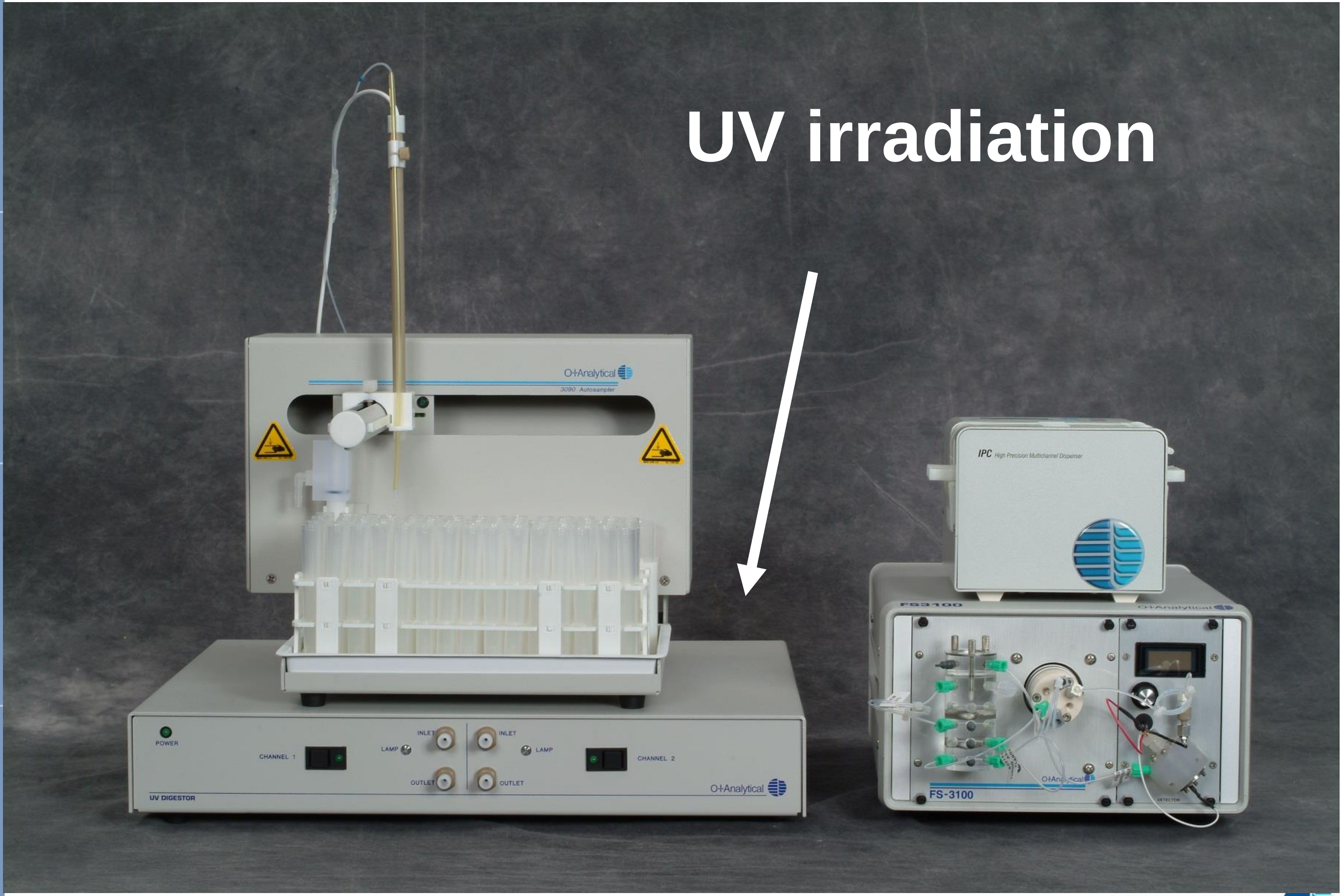
The CNSolution is your solution to cyanide analysis

- **Gas diffusion amperometry methods:**
  - Save time
  - Save money
  - Are more accurate
  - Have fewer interferences
  - Are "green"
- **The CNSolution = the FS3100**
  - Change to a photometric detector and run any colorimetric chemistry

The CNSolution 3100 available cyanide system



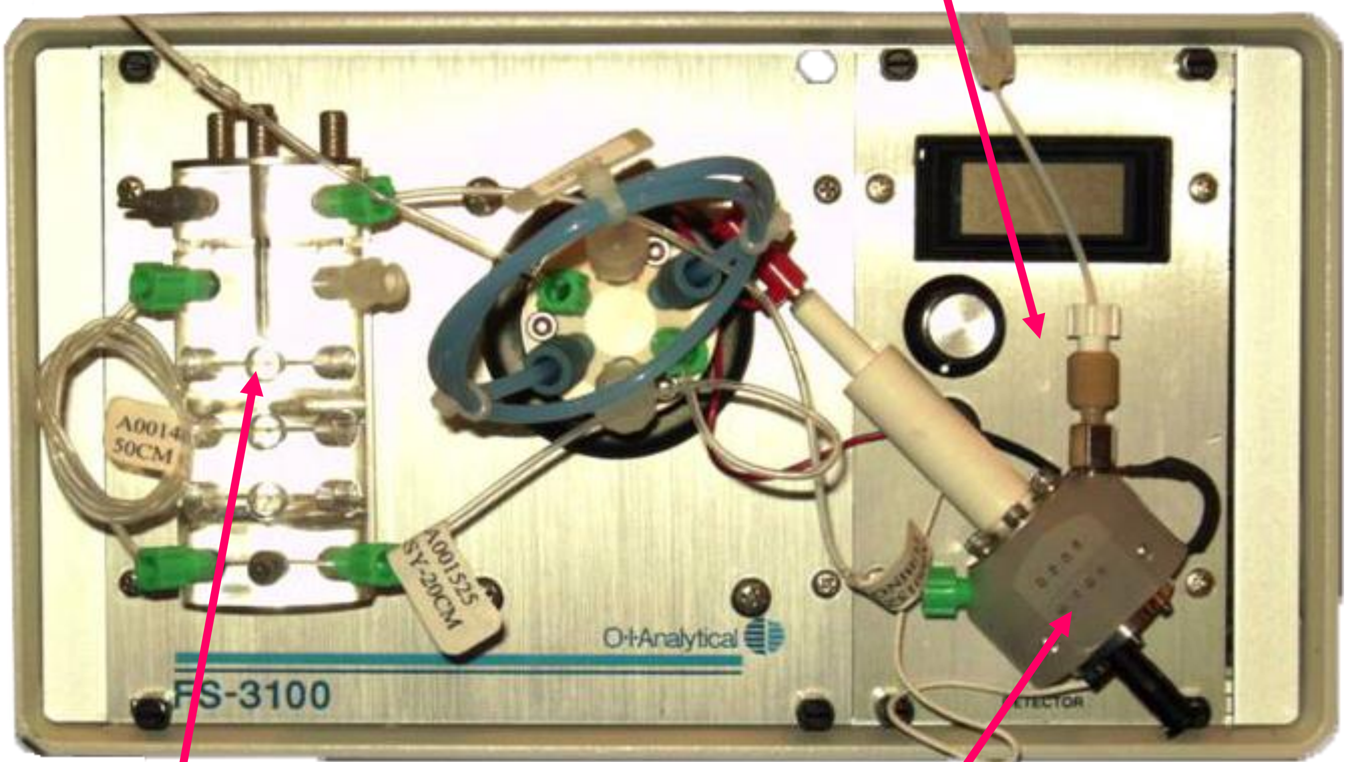
The CNSolution 3100 total cyanide system



O·I·Analytical

OIA 1677 - CNSolution

Detector



Gas Diffusion and Mixing

Flow-cell

O·I·Analytical

Flow Solution 3100

- Flow Injection Analyzer
  - Colorimetric detector added it becomes the FS 3100 FIA analyzer
  - All FS 3100 methods
    - NO_3-N
    - NH_3-N
    - PO_4
    - TKN

O·I·Analytical

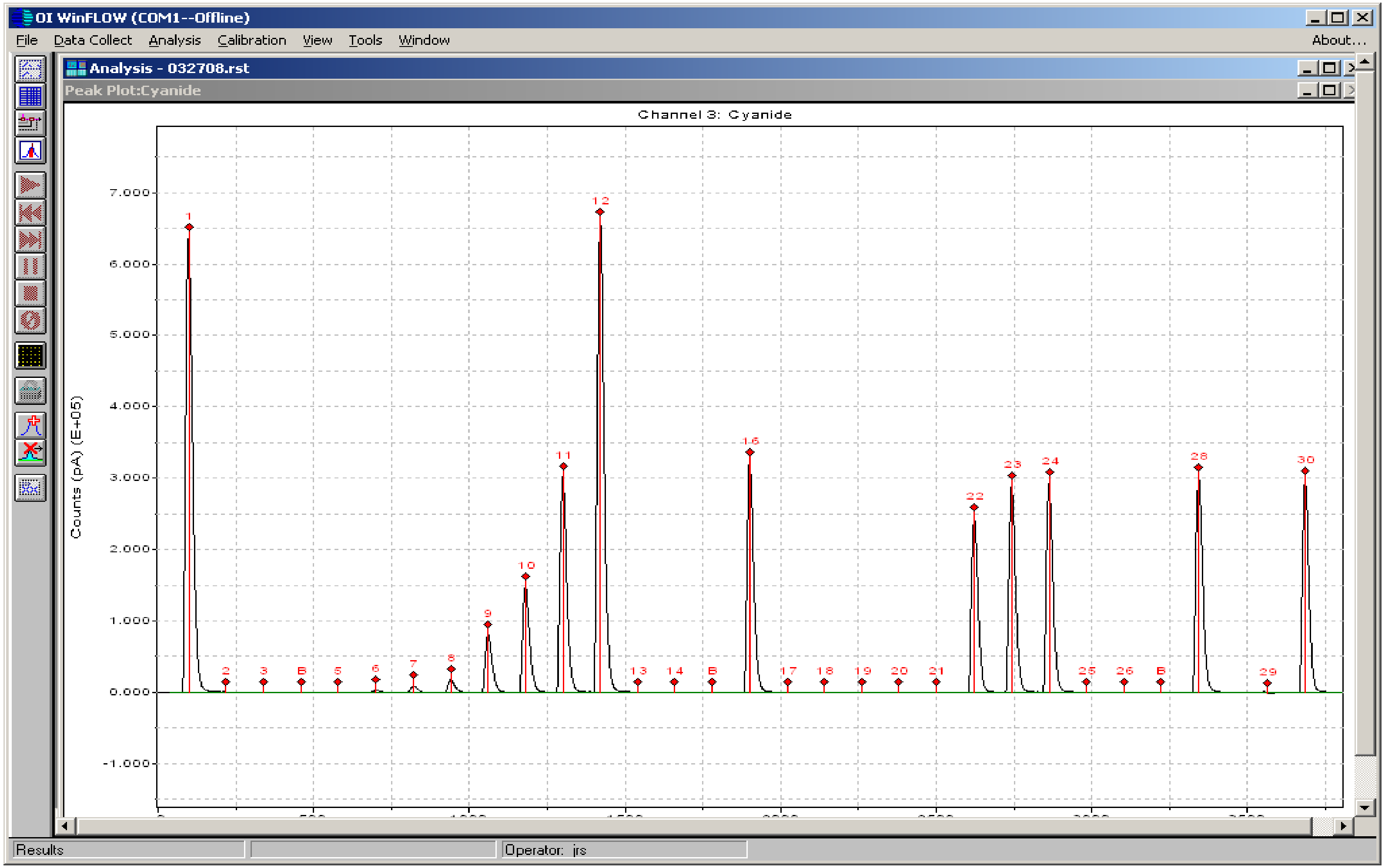
A high quality peristaltic pump

Separate module, individual channels, long pump tube life.

A random access xyz sampler

- Integrated circulating wash station
- 90 or 360 positions
- Separate standard and QC vials

Winflow software provide accurate quantitation of CN results



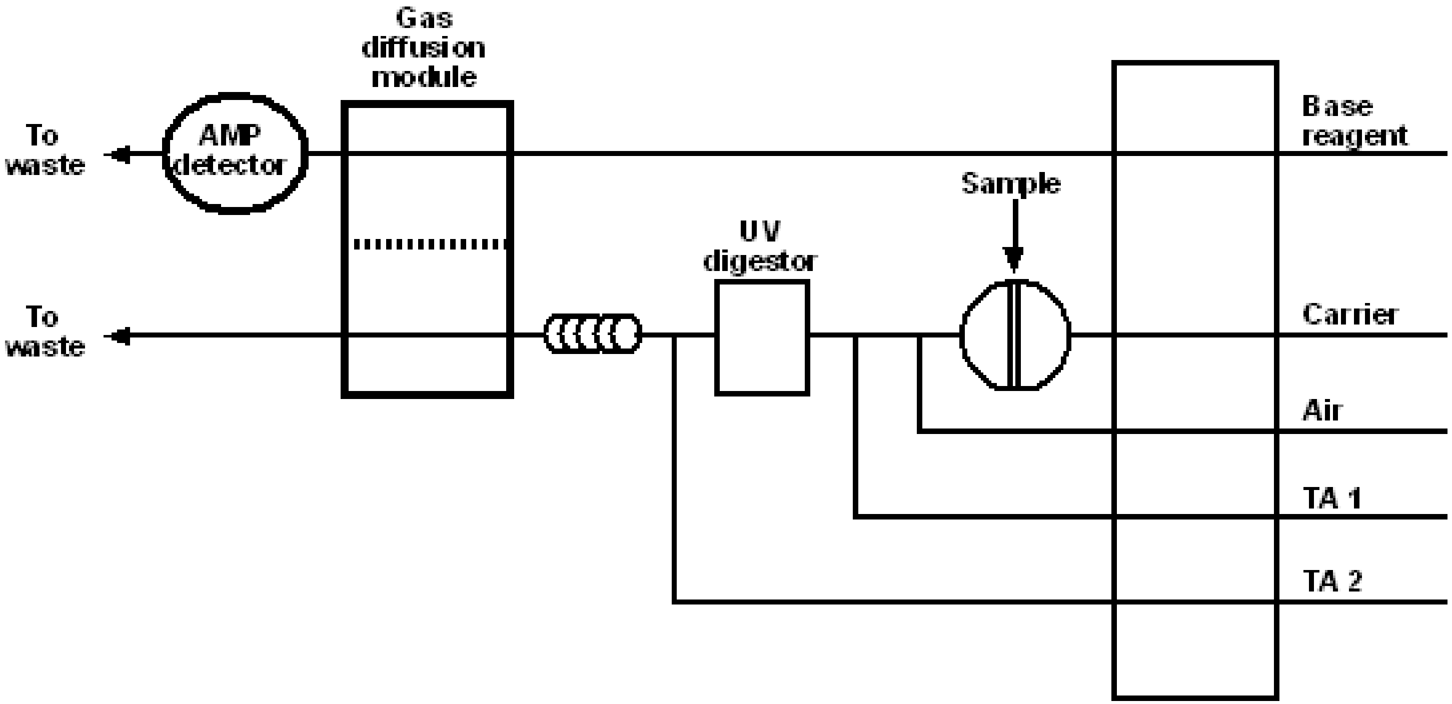
O·I·Analytical

The CNSolution 3100 is accurate, and cost effective

- Rapidly analyze cyanide
- Eliminate time consuming error causing distillations
- Expand capability to colorimetric FIA and SFA

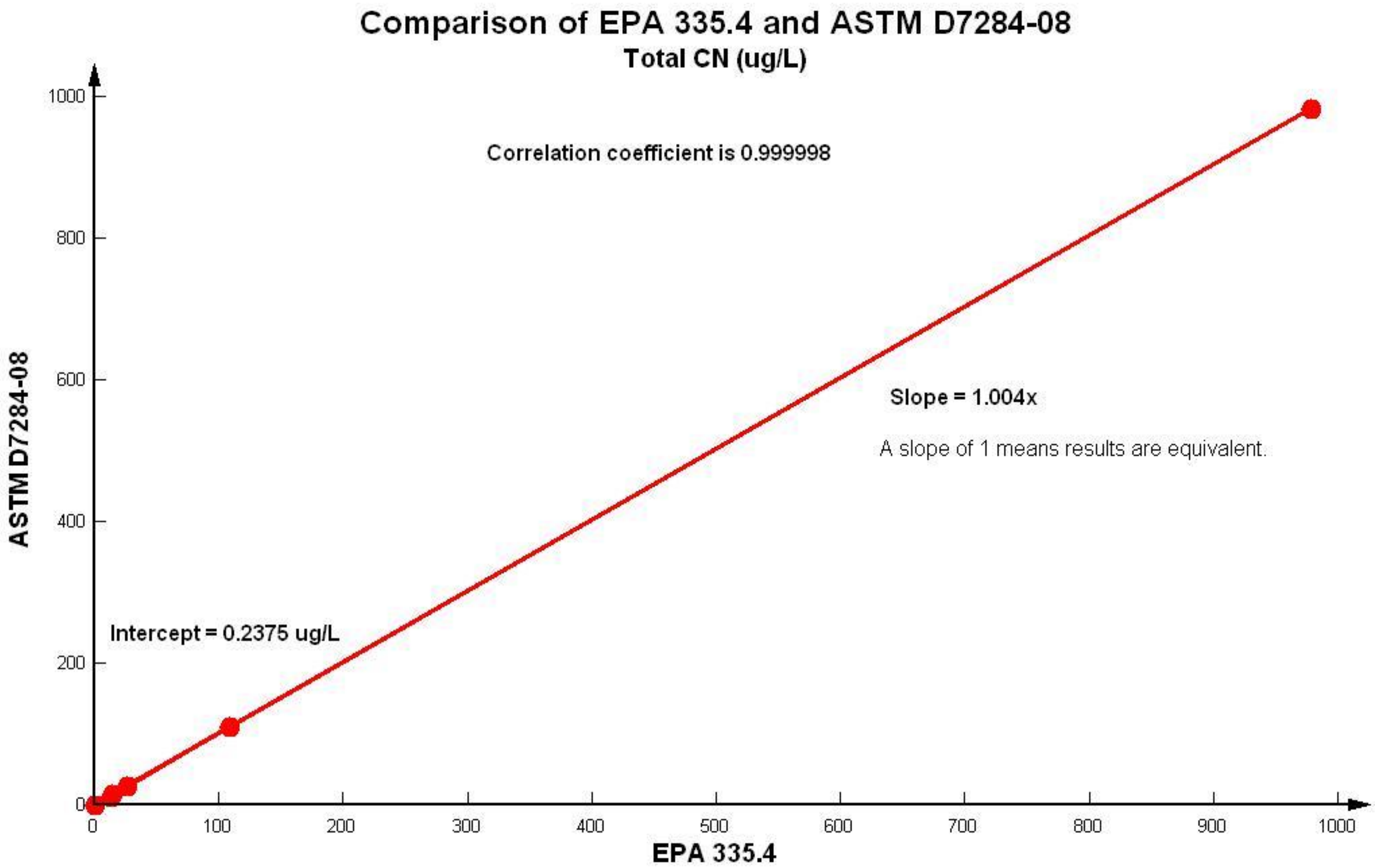
ASTM D7511 is easy to understand and operate and does not distill.

No pyridine

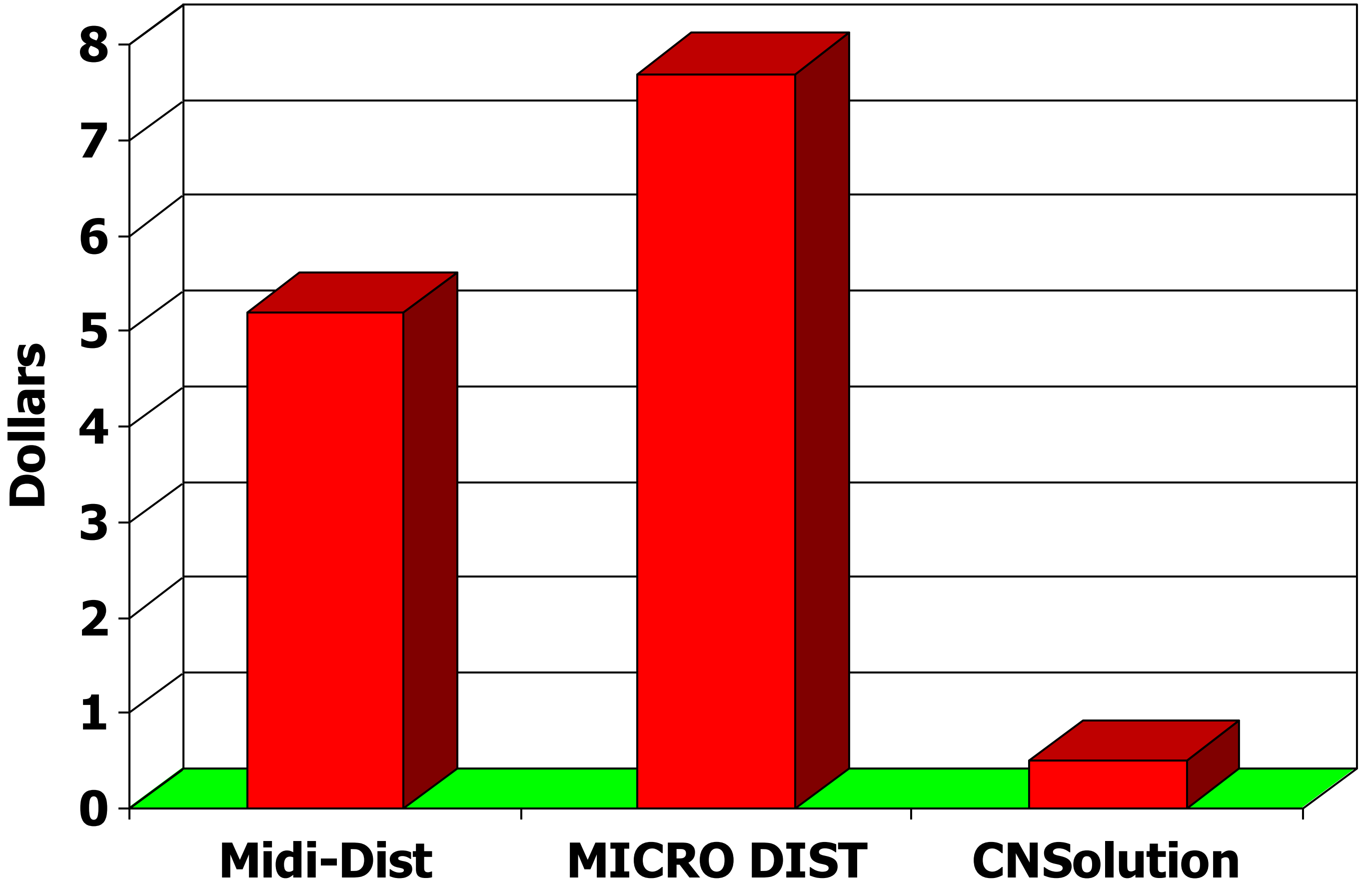


“Green” Chemistry

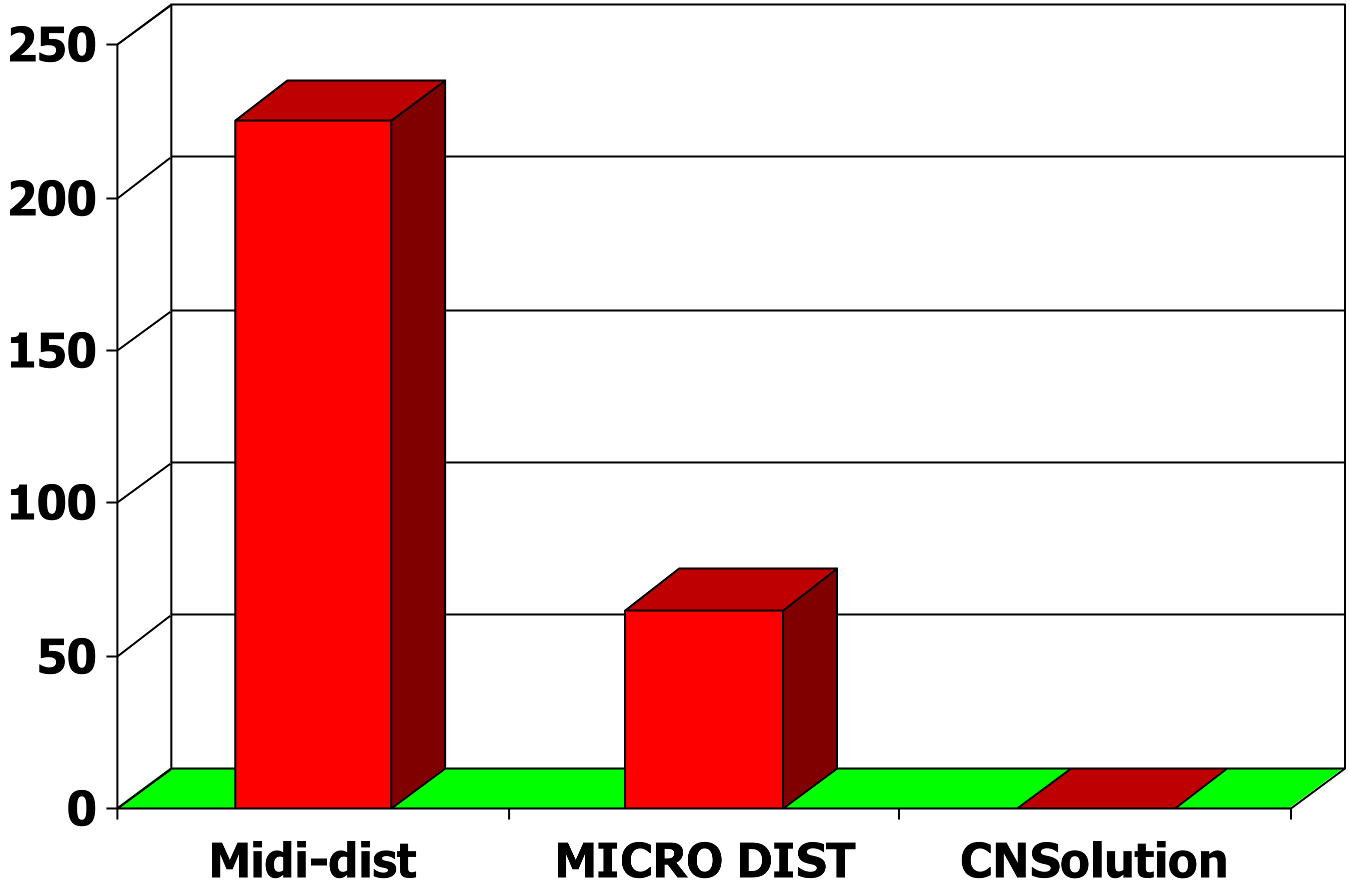
GD-Amperometry Equivalent to Colorimetry



Estimated Reagent and Consumable Cost per Analysis for Distillation (US Dollars)

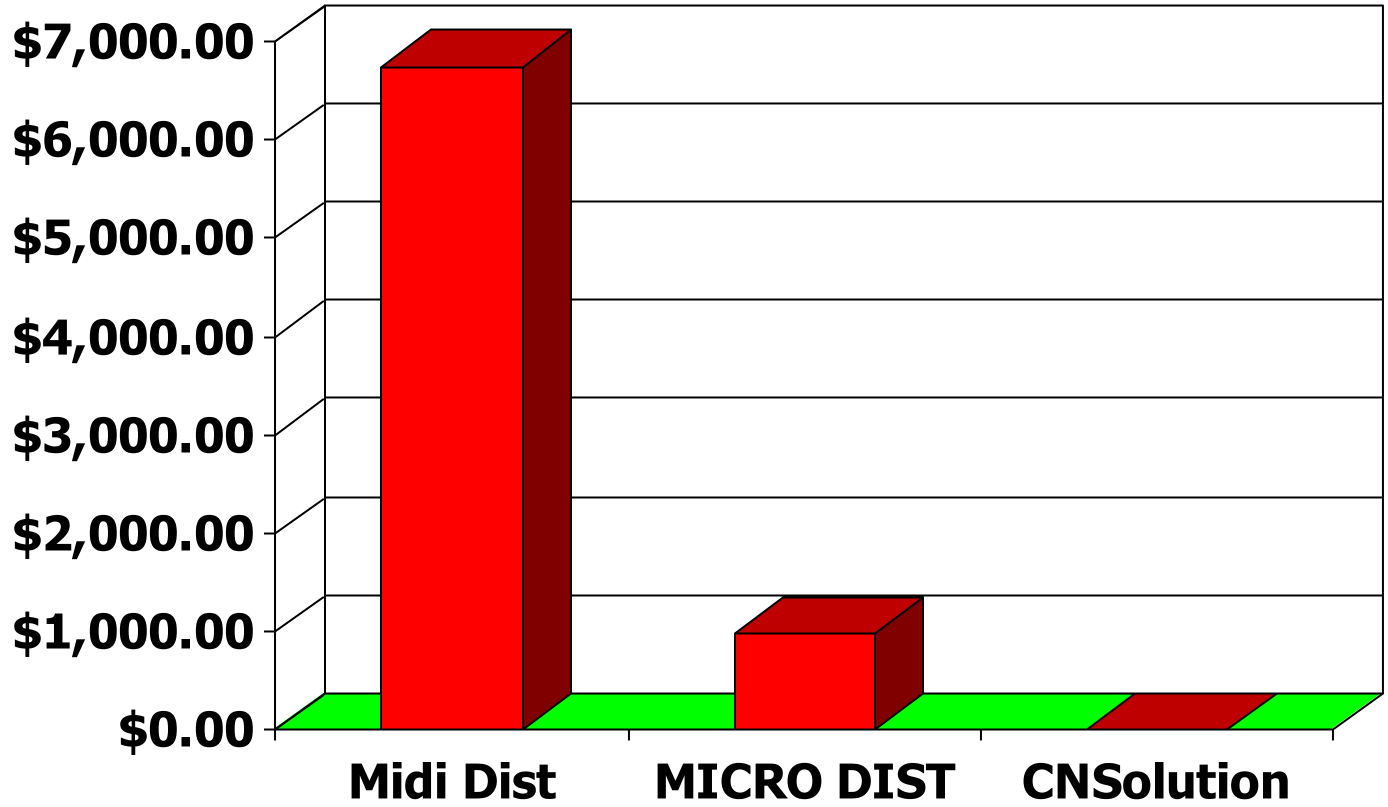


Estimated Labor (in minutes) Required to Distill 20 Samples for Analysis



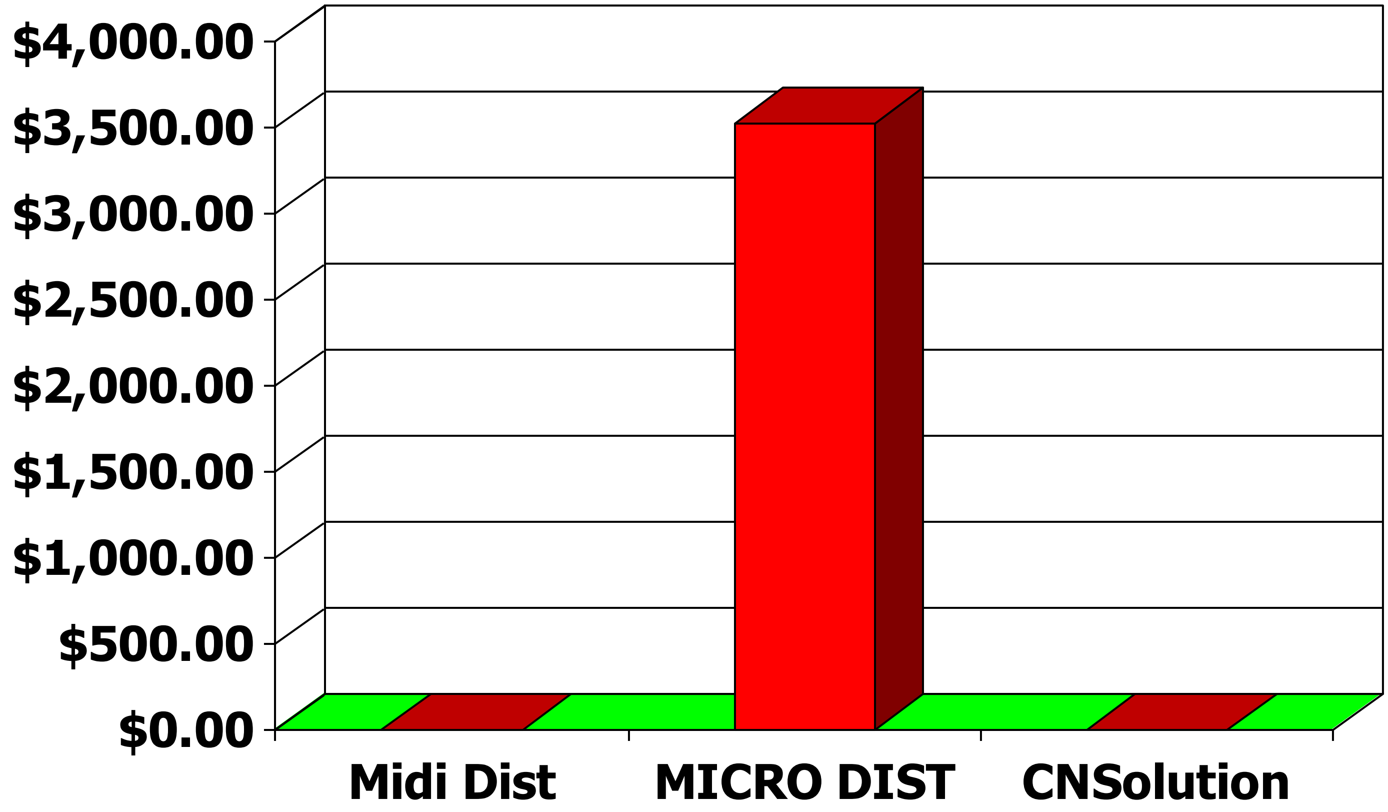
O·I·Analytical

Estimated Annual Labor Cost to Distill and Analyze 40 Samples per Month (Including Overhead)

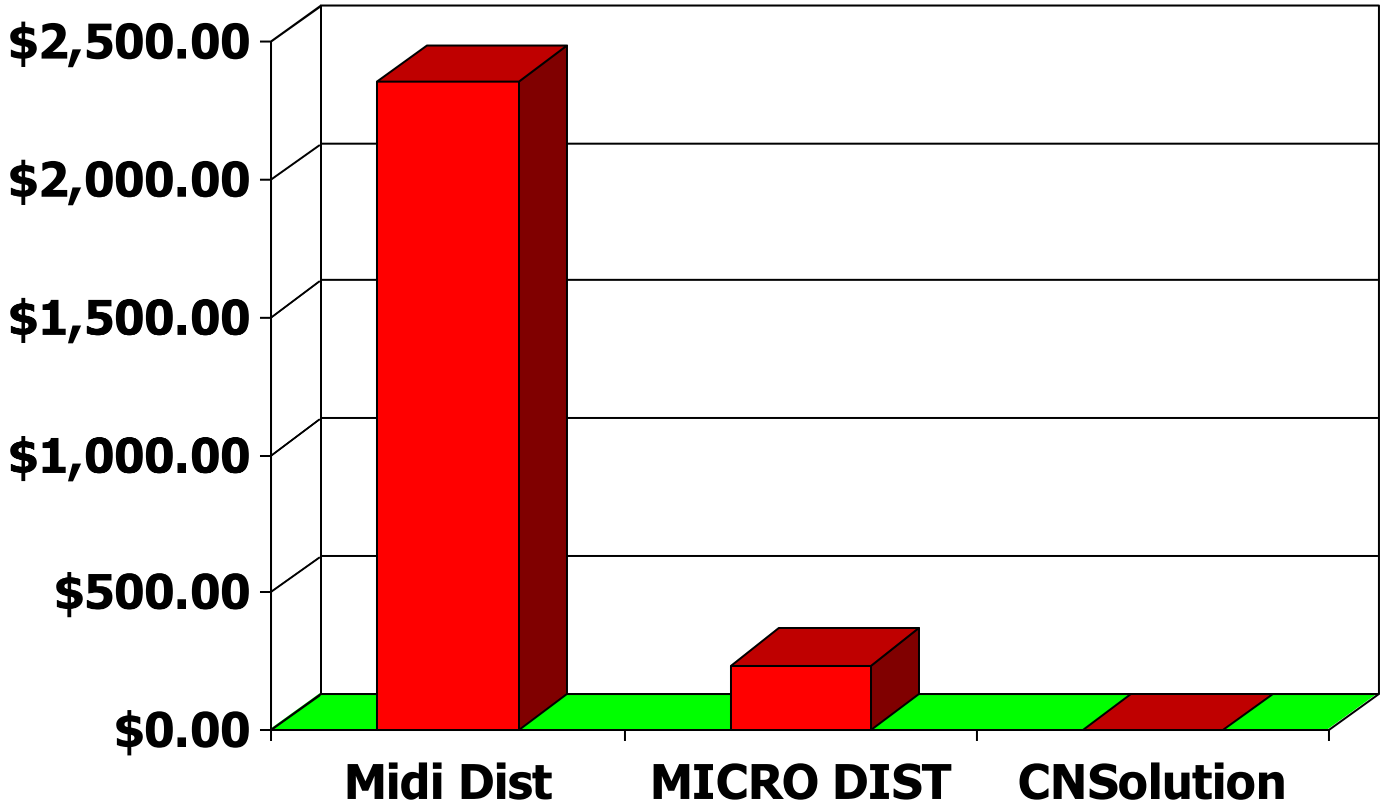


Assume tech pay at $15/hour

Estimated Annual Cost for Consumables to Distill and Analyze 40 Samples per Month

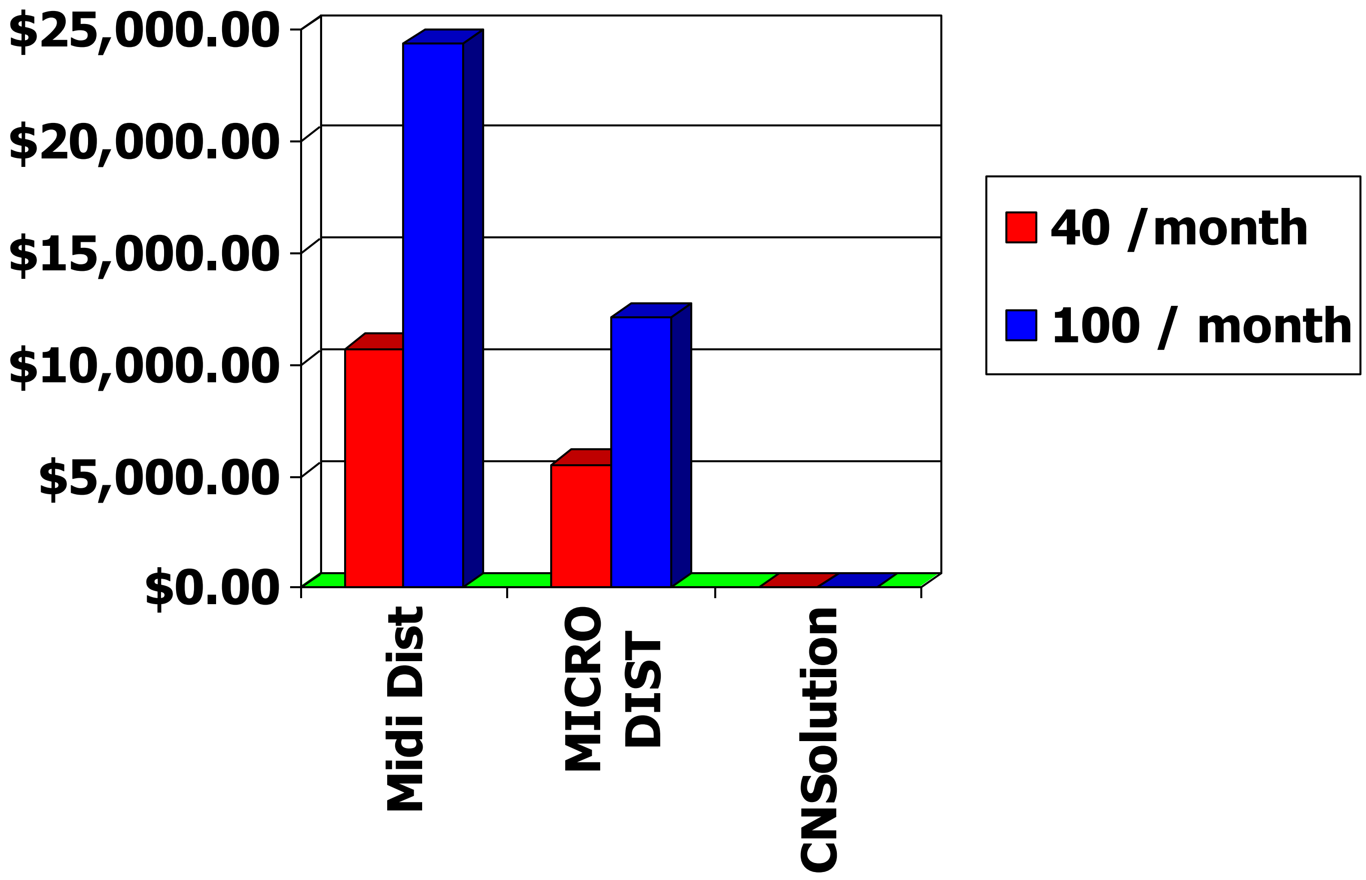


Estimated Annual Cost for Reagents to Distill and Analyze 40 Samples per Month

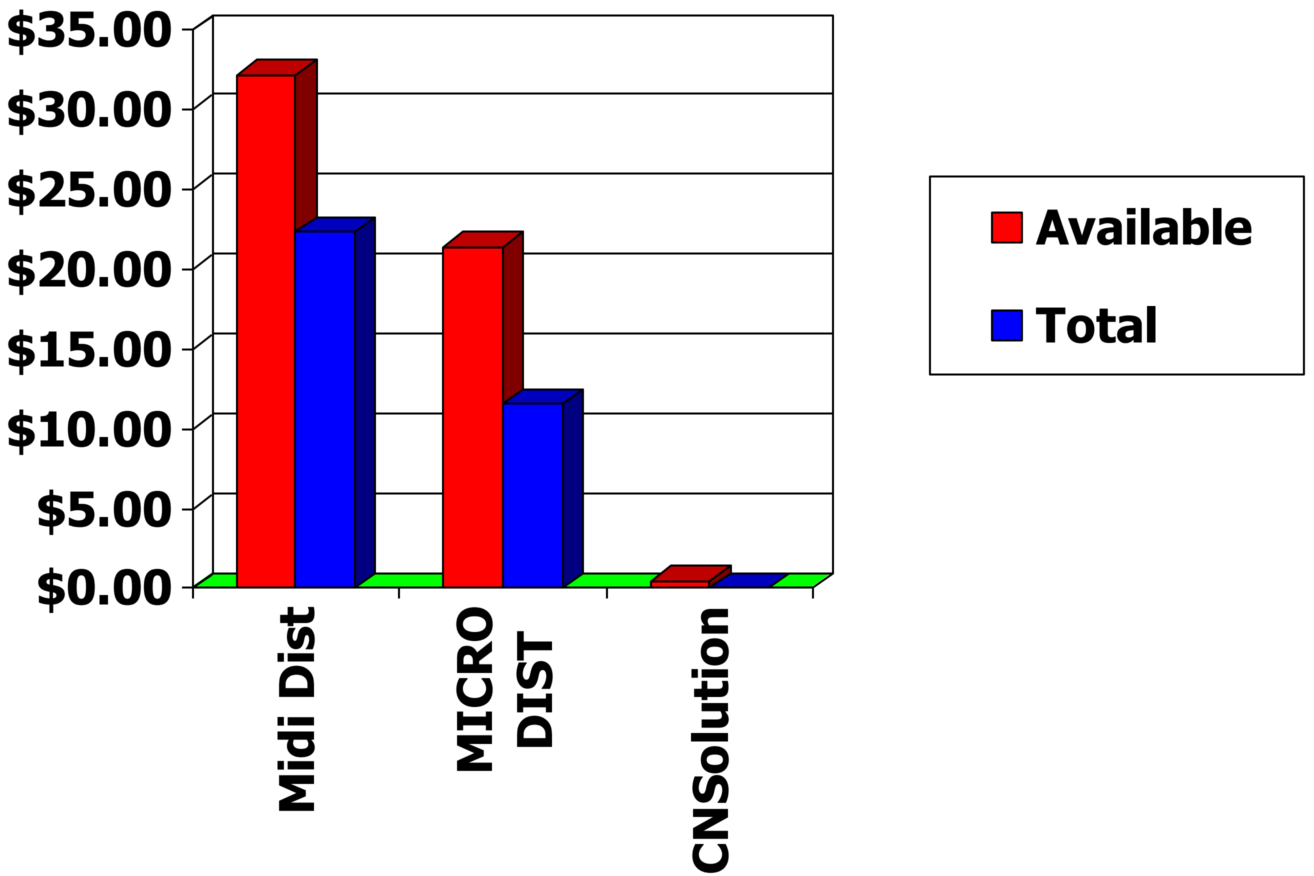


O·I·Analytical

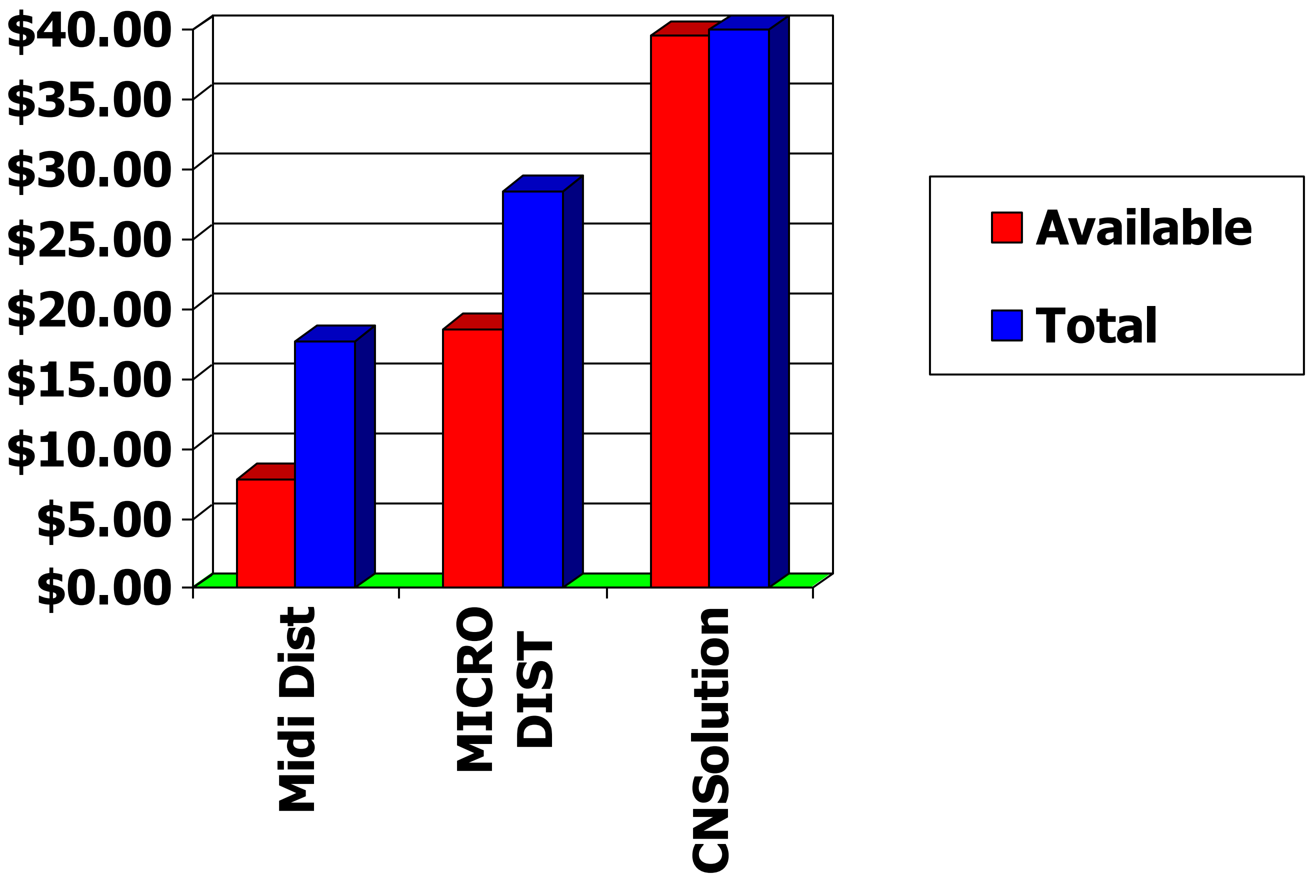
Annual Cost for Distillation vs. Non-Distillation Techniques



Comparison of Cost per Sample by Cyanide Species and Method

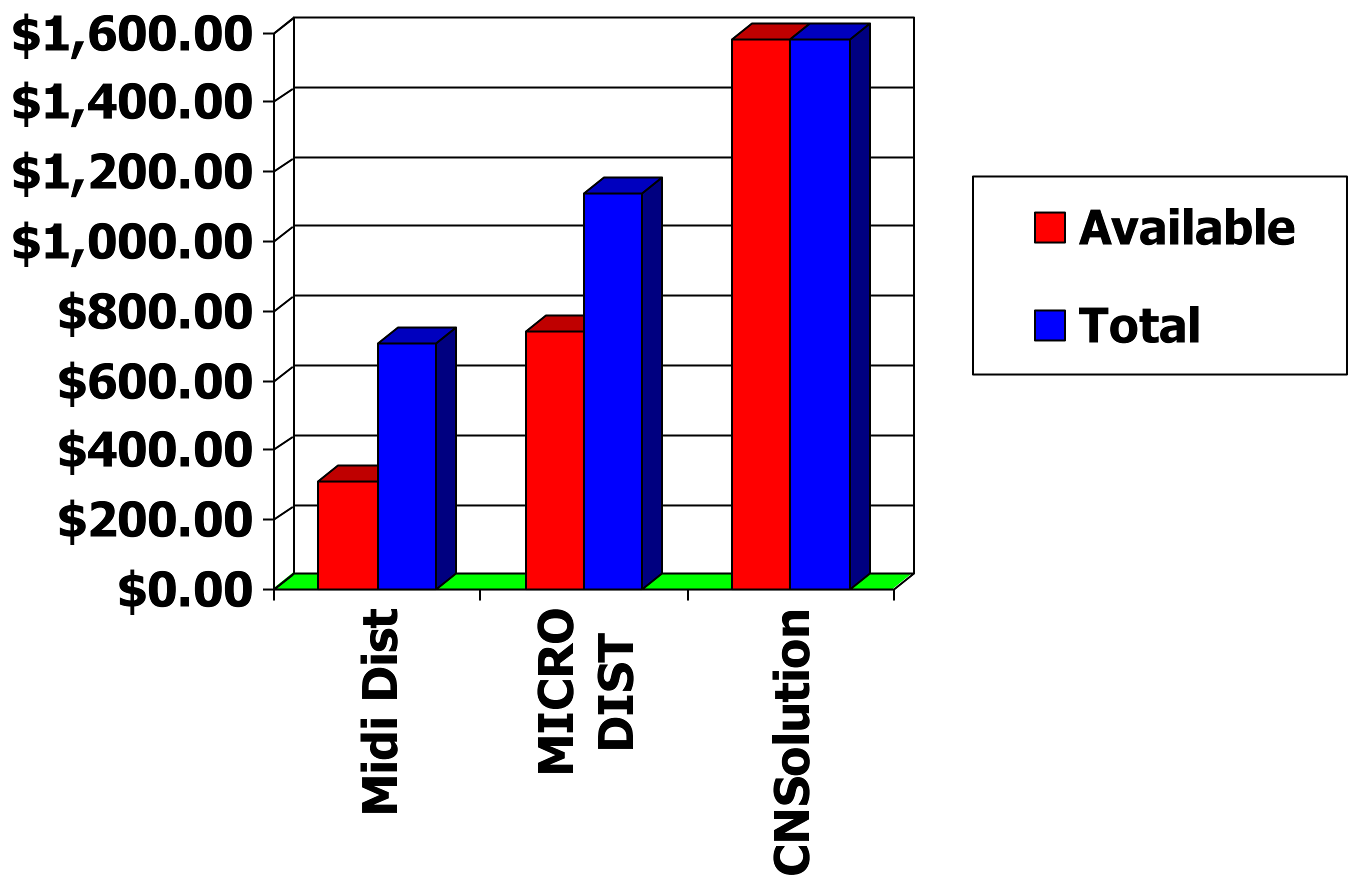


Profit per Sample by Cyanide Species at $40 per Test



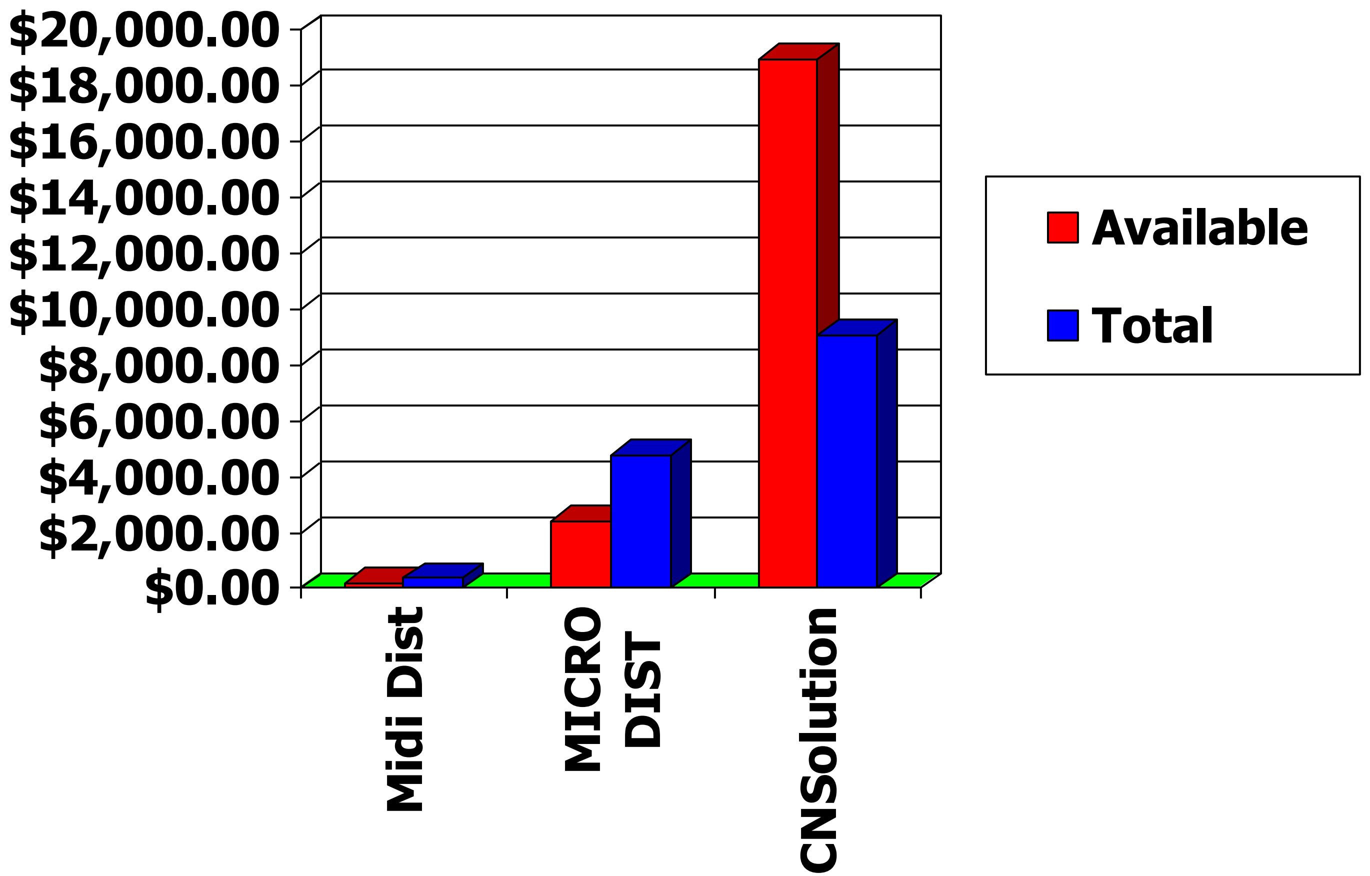
O·I·Analytical

Profit per Month by Cyanide Species at $40 per Test and 40 Samples per Month

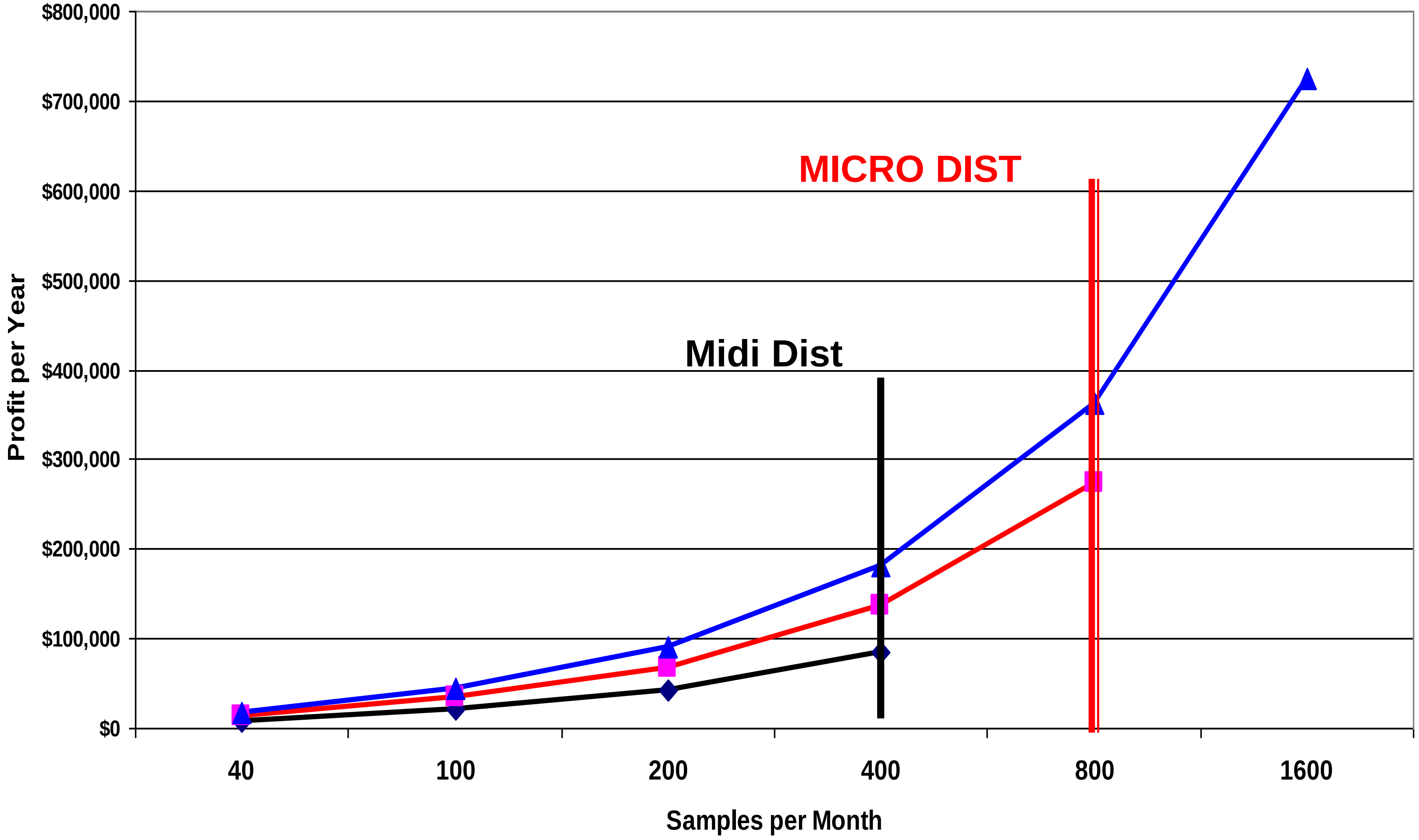


O·I·Analytical

Profit per Shift by Cyanide Species at $40 per Test Based on Maximum Capacity



Estimated Profit by Number of Samples Analyzed at Maximum Capacity

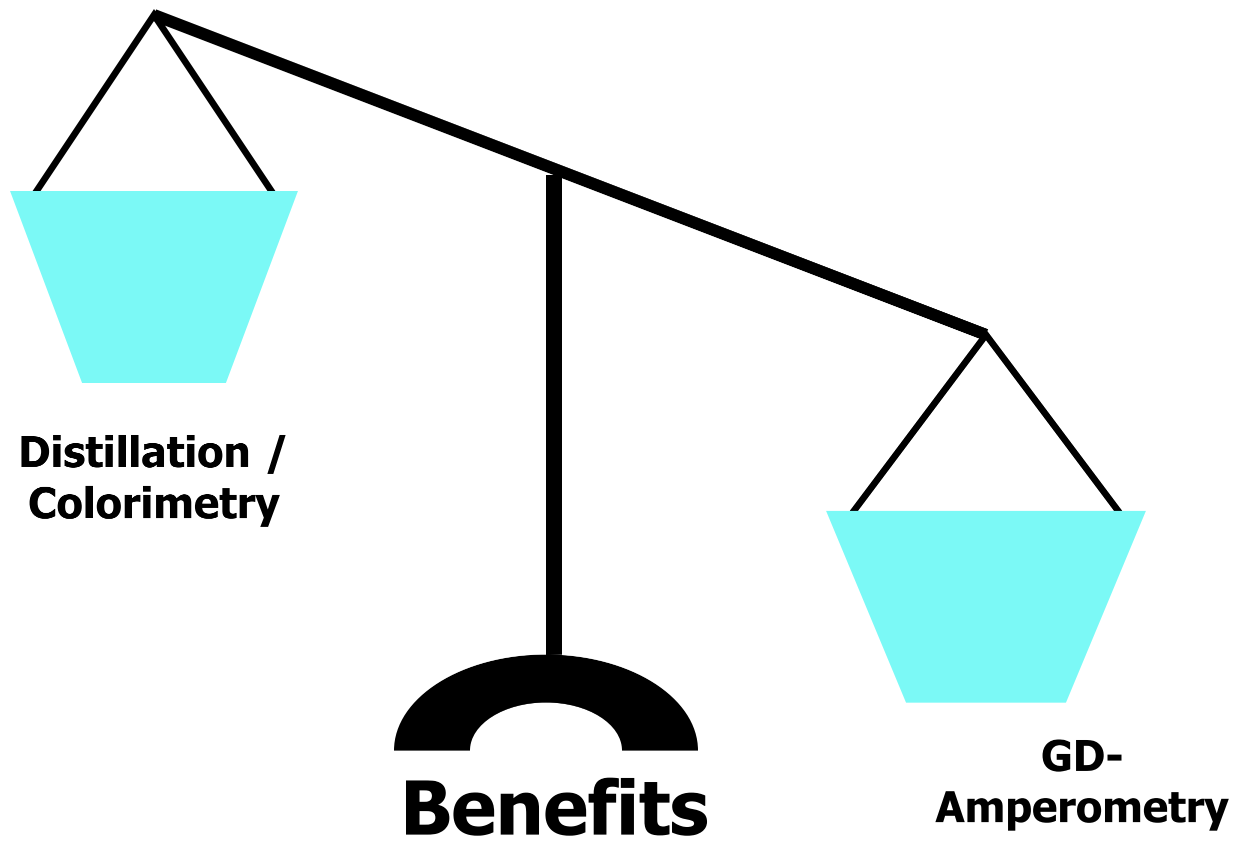


O·I·Analytical

Thoughts Regarding "Break Even" Analysis

- **Manual distillation and manual spectrometer versus CNSolution**
  - **Manual equipment costs 3 x less**
  - **CNSolution profit 3 x higher per test**
- **Break Even = 1000 samples for both!**
- **That's 20 samples per week regardless**

In summary, distillation/colorimetry should be replaced



Thank You

Questions?

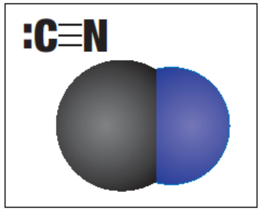
www.oico.com

An Overview and Comparison of Methods for Cyanide Analysis

Presented at the 2009 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Chicago, Illinois March 8, 2009–March 13, 2009

Introduction

Cyanide analysis methods attempt to measure groups of compounds with similar chemical characteristics and report them as a single value. Various techniques are employed to separate specific types of cyanide complexes from each other and potential matrix interferences to achieve accurate quantitation (Figure 1).



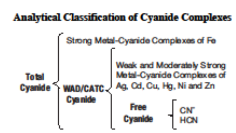


Figure 1. Cyanide refers to a monovalent anion consisting of carbon and nitrogen atoms with triple covalent bonds. Cyanide is very reactive and readily forms metal–cyanide complexes and organic compounds

O·I·Analytical

The regulated community is presented with an array of conflicting definitions of cyanide species, which leads to misunderstandings about what the various techniques and methods actually measure. In fact, the U.S. EPA *Solutions to Analytical Chemistry Problems with Clean Water Act Methods* [1], or "Pumpkin Guide", states; "Next to oil and grease, cyanide is the pollutant for which the most matrix interferences have been reported to EPA."

This study presents an overview and assessment of the most commonly used cyanide analysis methods including cyanide species measured, analytical techniques employed, potential matrix interferences, and final determinative steps.

Commonly Used Cyanide Analysis Methods

Free Cyanide

Free cyanide refers to the sum of hydrogen cyanide (HCN) and cyanide ion (CN^-) in a sample [2, 3]. Free cyanide is bioavailable and approximately a thousand times more toxic to aquatic organisms than it is to humans [4]. Analytically, free cyanide is referred to as the amount of HCN liberated from solution at pH 6.0.

Weak to Moderately Strong Metal – Cyanide Complexes

Weak to moderately strong metal-cyanide complexes are compounds that dissociate and release hydrogen cyanide gas under mildly acidic conditions (pH 3 to 6). Cyanide species within this category include: simple cyanides–soluble/dissociable alkali metal and alkali earth metal-cyanide complexes (NaCN, KCN, $Ca(CN)_2$); weak metal-cyanide complexes ($Zn(CN)_4^{2-}$, $Cd(CN)_3^-$); and moderately strong metal-cyanide complexes ($Cu(CN)_2^-$, $Ni(CN)_4^{2-}$, $Ag(CN)_2^-$) [2,3]. Weak Acid Dissociable (WAD), Cyanide Amenable to Chlorination (CATC), and Ligand Exchange methods were developed to quantify the sum of these cyanide species as well as any free cyanide present in a sample.

Methods intended to measure weak to moderately strong metal–cyanide complexes also measure simple cyanides. Simple cyanides include free cyanide, alkali metal cyanides, alkali earth metal cyanides, and ammonium cyanide.

Strong Metal-Cyanide Complexes

Strong metal-cyanide complexes are compounds that require strongly acidic conditions ($pH < 2$) to dissociate and release hydrogen cyanide gas [2]. Examples of strong metal-cyanide complexes include $Fe(CN)_6^{2-}$, $Fe(CN)_6^{4-}$, $Co(CN)_6^{4-}$, and $Au(CN)_2^-$. The strong acidic conditions used to dissociate these resistant metal-cyanide complexes readily dissociates all other cyanide species present in a sample. "Total Cyanide" is the term used in U.S. EPA methods to refer to the sum of all cyanide species that are converted to hydrogen cyanide following reflux distillation of a sample acid in a strong solution.

For a summary of cyanide analysis methods, refer to Table 1 .

Table 1: Summary of CN Analysis Methods

Description Name	Method	Description	Potential Interferences	Measurement
Free Cyanide	ASTM D 4282	Passive Diffusion at pH 6 and room temperature	• Storage • Measurement	• Manual chlorination of cyanide with chloramine-T and subsequent reaction with pyridine-barbituric acid. • Maximum absorbance is determined by manual colorimetry.
	ASTM D 7237	Flow Injection Analysis (FIA) into a reagent at a pH of 6–8	• Storage • Measurement	Gas Diffusion-Amperometry
Available Cyanide (CATC) (WAD)	SM 4500-CN G ASTM D2036	• Alkaline-Chlorination to destroy all weak and dissociable metal-cyanide complexes and any free or simple cyanide. • Two manual distillations (total-chlorinated)=CATC	• Excessive light, ammonia. • Incomplete recovery on Ag-cyanide complexes. • Storage • Distillation • Measurement	• Manual chlorination of cyanide with chloramine-T and subsequent reaction with pyridine-barbituric acid. • Maximum absorbance is determined by manual colorimetry.
	ASTM D2036	Buffered (pH 4.5) manual distillation	• Excess of Fe-cyanide complexes. • Incomplete recovery on Hg-cyanide complexes. • Storage • Distillation • Measurement	• Manual chlorination of cyanide with chloramine-T and subsequent reaction with pyridine-barbituric acid. • Maximum absorbance is determined by manual colorimetry. Manual Ion Selective Electrode (ISE), Titration.
	ASTM D4374 Kelada 01	Buffered (pH 4.5) automated flash distillation	• Storage • Distillation • Measurement	• Automated chlorination of cyanide with chloramine-T and subsequent reaction with pyridine-barbituric acid. • Automated colorimetry
	OIA 1677 ASTM D6888	Pretreatment with ligand exchange reagents, room temperature automated gas diffusion.	• Storage • Measurement	Amperometry
Total Cyanide	SM 4500 CN D SM 4500 CN E	• Cyanide ion is released from cyanide complexes as HCN by means of macro manual reflux-distillation in the presence of a strong sulfuric acid solution and magnesium chloride. • The HCN is swept into a dilute sodium hydroxide absorber solution.	• Storage • Distillation • Measurement • Excessive Light	SM 4500 CN D: Cyanide in the absorber solution is titrated with silver nitrate. SM 4500 CN E: • Cyanide in the absorber solution is converted to cyanogen chloride by manual reaction with chloramine-T at pH <8. • After reaction, the cyanogen chloride forms a red-blue color on addition of pyridine-barbituric acid reagent. • Maximum color is determined by manual colorimetry.
	ASTM D2036	• Cyanide ion is released from cyanide complexes as HCN by means of a macro, or scaled down manual reflux-distillation in the presence of a strong sulfuric acid solution and magnesium Chloride. • The HCN is swept into a dilute sodium hydroxide absorber solution.	• Storage • Distillation • Measurement • Excessive Light	• Cyanide in the absorber solution is titrated with silver nitrate. • Cyanide in the absorber solution is determined manually by Ion Selective Electrode (ISE). • Cyanide in the absorber solution is converted to cyanogen chloride by manual reaction with chloramine-T at pH <8. • After reaction, the cyanogen chloride forms a red-blue color on addition of a pyridine-barbituric acid reagent. • Maximum color is determined by manual colorimetry.
	EPA 335.4	• Cyanide ion is released from cyanide complexes by means of a scaled down (midi) manual reflux-distillation in the presence of a strong sulfuric acid solution and magnesium chloride. • The HCN is swept into a dilute sodium hydroxide absorber solution.	• Storage • Distillation • Measurement • Excessive Light	• Cyanide in the absorber solution is converted to cyanogen chloride by automated reaction with chloramine-T at pH <8. • After reaction the cyanogen chloride forms a red-blue color on addition of a pyridine-barbituric acid reagent. • Maximum color is determined by automated colorimetry.
	Kelada 01, ASTM D4374, EPA 335.3	• Cyanide ion is released from cyanide complexes by means of UV irradiation and automated flash distillation in the presence of a strong sulfuric acid solution. • The HCN generated is injected into an auto chemistry analyzer chemistry cartridge.	• Storage • UV Irradiation • Distillation • Measurement	• Cyanide in the absorber solution is converted to cyanogen chloride by automated reaction with chloramine-T at pH <8. • After reaction, the cyanogen forms a red-blue color on addition of a pyridine-barbituric acid reagent. • Maximum color is determined by automated colorimetry.
	ASTM D7284	• Cyanide ion is released from cyanide complexes by means of a scaled down (midi) manual reflux-distillation in the presence of a strong sulfuric acid solution and magnesium chloride. • The HCN is swept into a dilute sodium hydroxide absorber solution.	• Storage • Distillation • Measurement	Cyanide in the absorber solution is determined by automated gas diffusion amperometry.
	OIA 1678/ASTM D7511-09	• Cyanide ion is released from cyanide complexes by UV irradiation. • The HCN generated diffuses across a membrane and is measured amperometrically.	• Storage • UV Irradiation • Measurement	Cyanide is determined by automated gas diffusion amperometry.

Potential Method Interferences

Sampling, Preservation, and Storage Interferences

Certain interferences occur during the sampling, preservation, and storage process and apply, to some extent, to all cyanide methods. Chemical preservatives added to samples to preserve the original concentration of cyanide in the sample need to be chosen according to the analytical method that will be used. In general, distillation methods are less forgiving and require extra care in sample pretreatment. Table 2 contains a summary of interferences that result from sample storage and preservation.

Sample Processing Interferences

The sample processing necessary to break metal-cyanide bonds and liberate the cyanide generated from the aqueous sample solution is not interference free. Often, in some sample matrices, the sample processing introduces so much doubt into the measurement that the results cannot be trusted at all. Table 2 contains a summary of interferences that can be introduced during sample processing.

Measurement Interferences

The final measurement technique used to determine the cyanide concentration is also not interference free. Since the final measurement is performed under the assumption that all interferences were previously removed, these interferences often go undetected. This is especially true for automated colorimetric methods. Table 2 contains a summary of interferences that may occur during the final cyanide measurement step.

Table 2: Summary of CN Method Interferences

Analysis Step	Compound	Process/Measurement Technique	Description of Interference
Sampling, Preservation, and Storage	Residual chlorine, peroxide, or other oxidizers	N/A	React with cyanide in solution rapidly decreasing the cyanide concentration. Oxidizers can co-exist with cyanide.
	Chloramines	N/A	React with sample at pH>10 increasing the cyanide concentration.
	Sulfide	N/A	Reacts with cyanide to form thiocyanite decreasing the cyanide concentration. Reaction is especially rapid if metal sulfides, such as lead sulfide, are present. The reaction is fairly slow without metal sulfides.
	Native Sulfur (colloidal sulfur)	N/A	Reacts with cyanide to form thiocyanate decreasing the cyanide concentration. Reaction is very fast with colloidal sulfur.
	Sulfite	N/A	Reacts with strong cyanide complexes at pH>10 decreasing the cyanide concentration. The reaction is almost immediate at pH>12.
	Light (<350 nm)	N/A	Reacts with strong metal-cyanide complexes releasing free cyanide.
	Ascorbic acid	N/A	Reacts with cyanide decreasing the cyanide concentration. Sample holding time when ascorbic acid is added is less than 48 hours. In some samples, ascorbic acid can react with ammonia or other nitrogen sources and increase the cyanide concentration.
	Formaldehyde	N/A	Reacts with cyanide decreasing the concentration. In some samples, formaldehyde reacts with ammonia or other nitrogen sources and increases the cyanide concentrations.
Sample Processing	Oxidizers	Distillation	Reacts with cyanide decreasing its concentration.
	Sulfide	Distillation	Distills into absorber solution and reacts with CN forming thiocyanate.
		Gas-diffusion	Passes through diffusion membrane.
	Sulfite (or Sulfur Dioxide)	Distillation	Reacts with cyanide decreasing its concentration. Distills into absorber solution and reacts with cyanide decreasing its concentration.
	Thiosulfate and other oxidized sulfur species (except sulfate)	Distillation	Decompose to form native sulfur and sulfur dioxide. React with cyanide decreasing its concentration. Sulfur Dioxide distills into absorber solution and reacts with cyanide decreasing its concentration.
	Thiocyanate	Cyanide Amenable to Chlorination (CATC)	Reacts with chlorine during alkaline chlorination and generates cyanide. Causes negative CATC results.
		Distillation	Decomposes to sulfur dioxide and reacts with cyanide decreasing its concentration. Sulfur dioxide distills into absorber solution.
		UV Irradiation	Can react at < 280 nm to form cyanide
	Thiocyanate + Nitrate or Nitrite	Distillation	Decompose to form cyanide
	Misc. Organics + Nitrate or Nitrite	Distillation	Decompose to form cyanide
	Carbonate	Distillation	Excessive foaming and possible violent release of carbon dioxide
		Gas diffusion	Passes through diffusion membrane
Measurement	Sulfide	Titration	Detected as cyanide
		Ion Selective Electrode	Detected as cyanide
		Colorimetry	Detected as cyanide (at > 10–mg S/L)
		GD-Amperometry	Detected as cyanide (at > 50–mg S/L)
	Thiocyanate	Colorimetry	Detected as cyanide
	Fatty Acids	Titration	Mask end point
	Sulfur Dioxide	Colorimetry	Increase chloramine-T demand resulting in a negative bias. The increased demand many not be noticed with automated methods.
	Carbonates	GD-Amperometry	Negative bias at > 1,500–mg CO_2/L

CN

NH_3

PO_4

NO_3

CN

NH_3

PO_4

NO_3