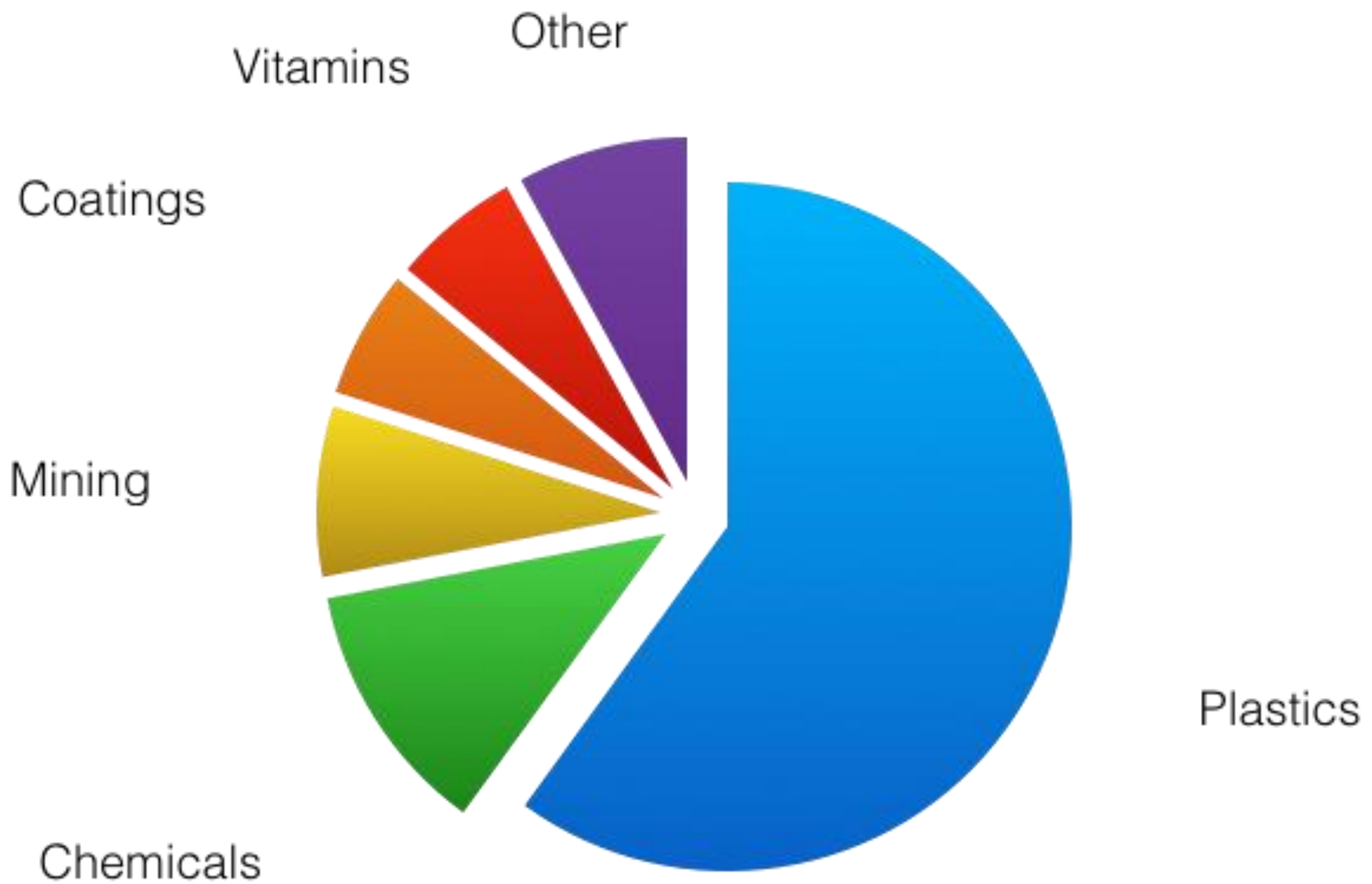
Cyanide Chemistry and Analysis

Contents

Fundamentals of CN Chemistry

Distribution of the Industrial Uses of CN

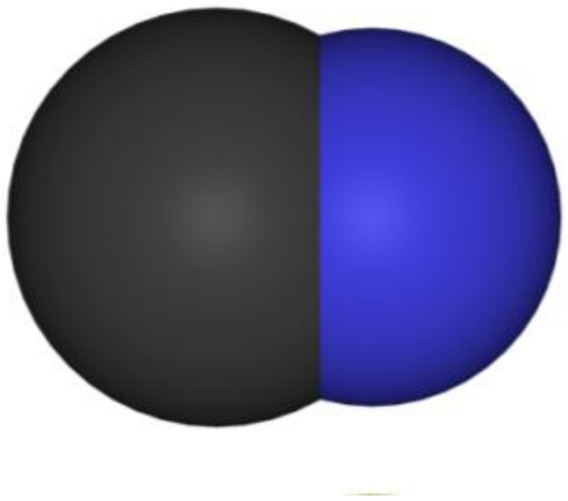


Who is measuring cyanide?

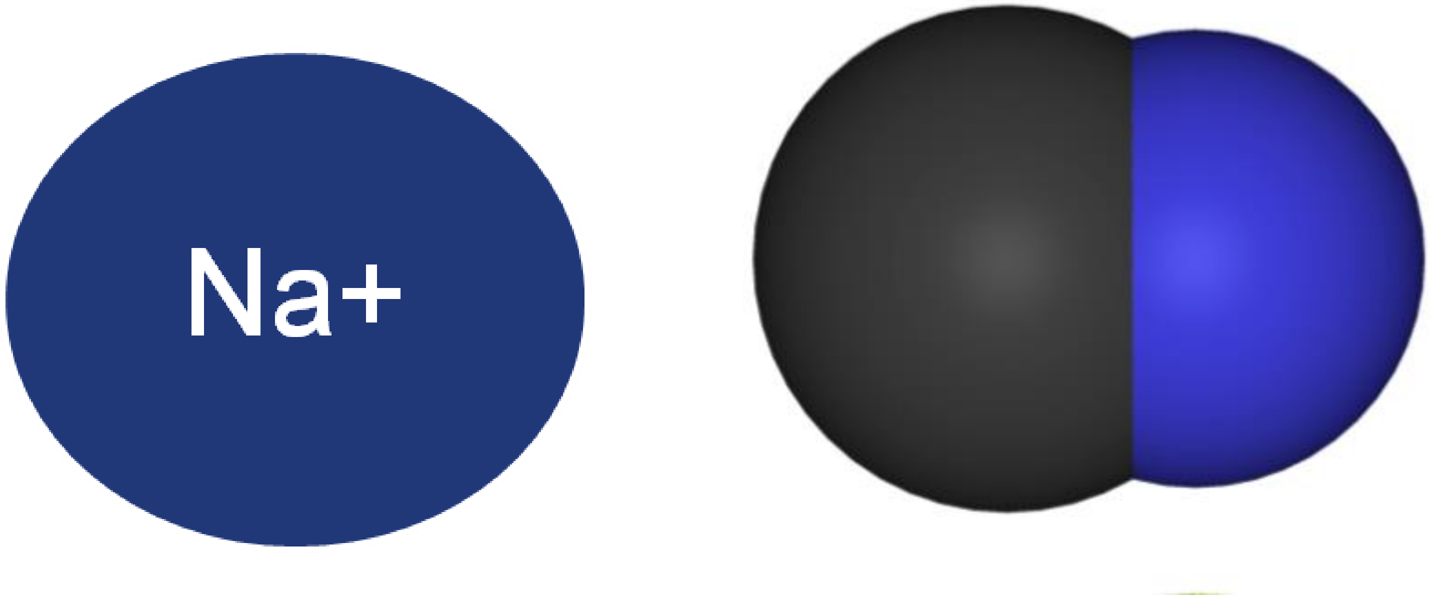
- **NPDES**
- **Pretreatment**
- **SDWA**
- **Industrial hygiene**
- **foods**
- **beverages**

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

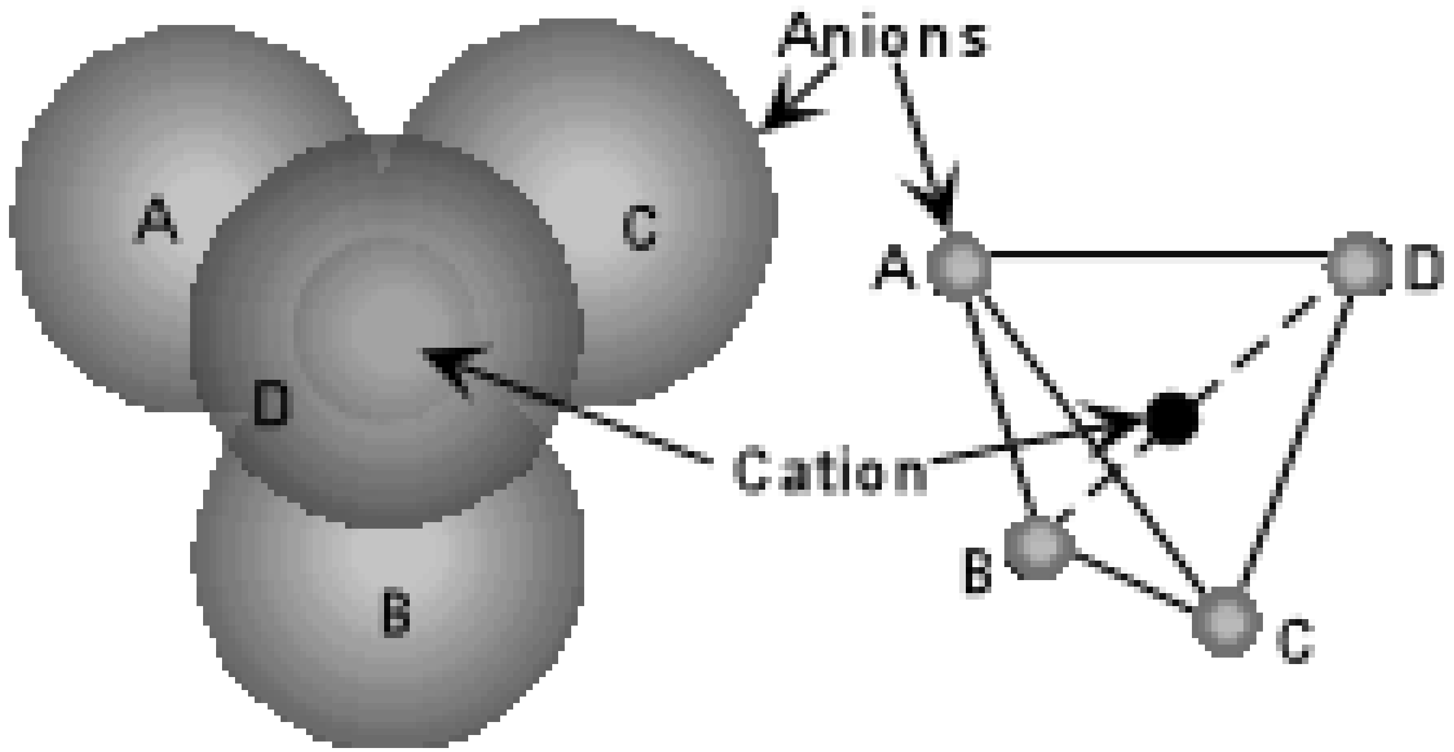
- **Transition metals - strong bonds**
- **Alkali metals - ionic bonds**



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

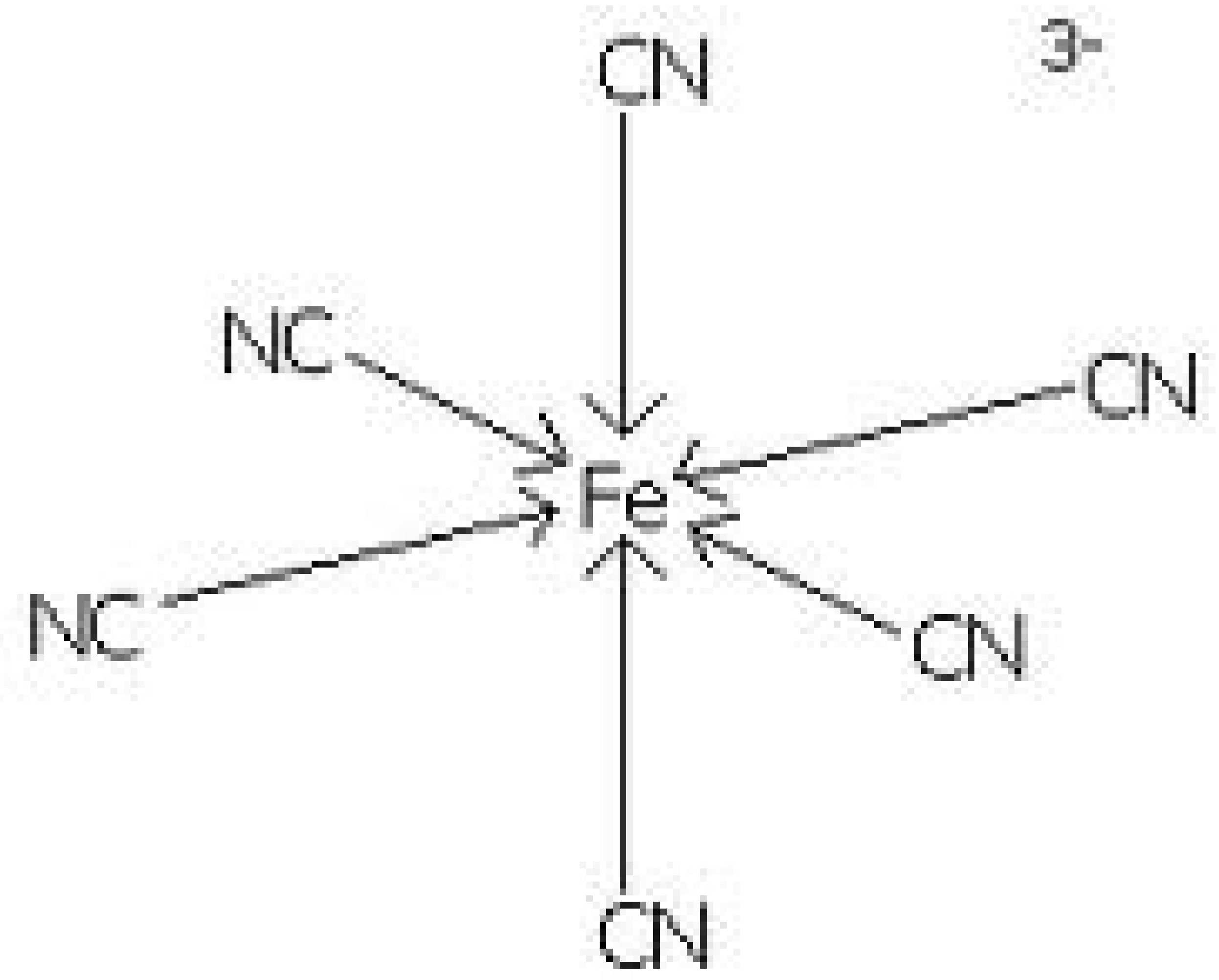


Metal Complexes require acid to generate HCN



Zn, Cd, Cu, Ni, Ag

Strong Metal Complexes are stable in acid solution



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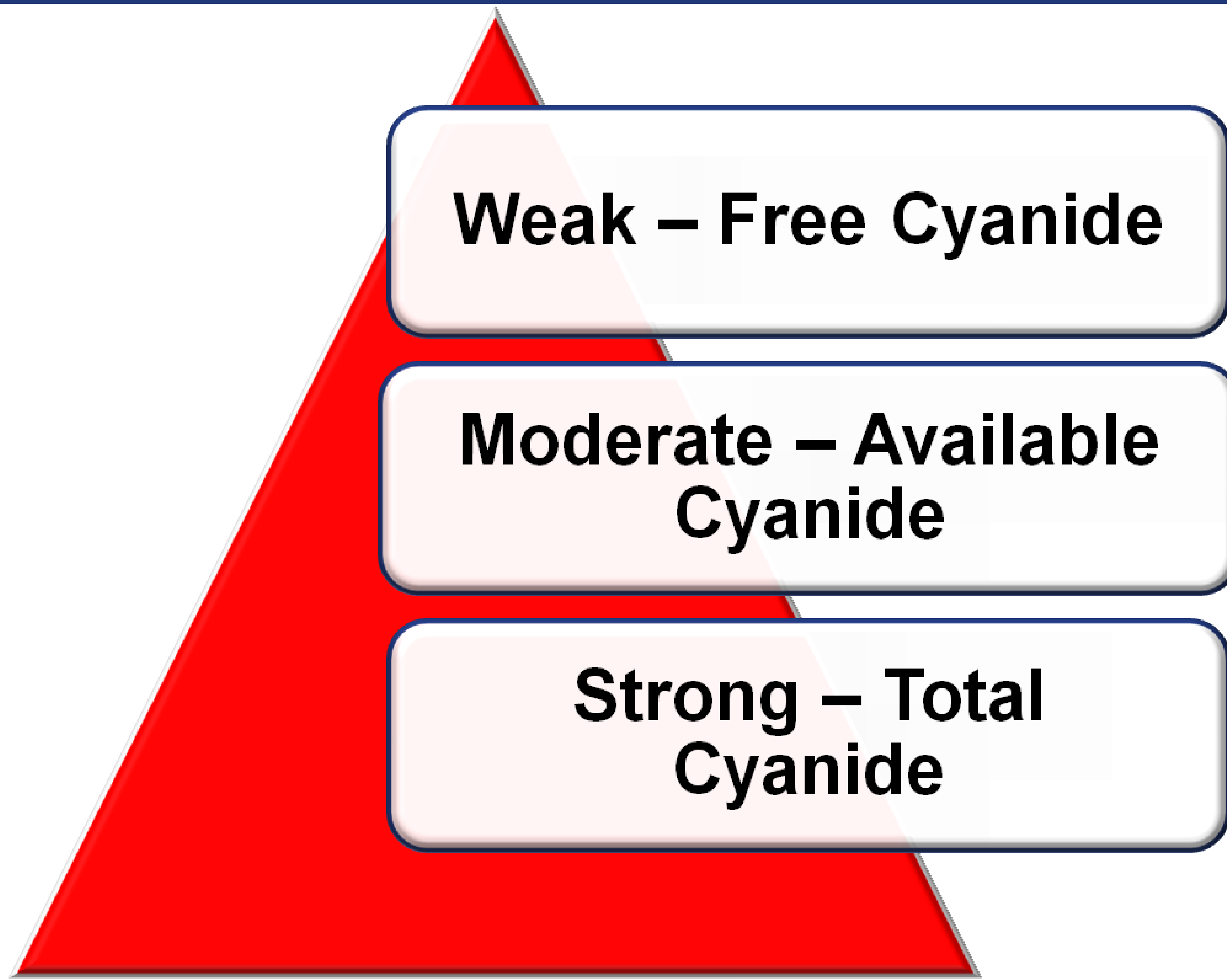
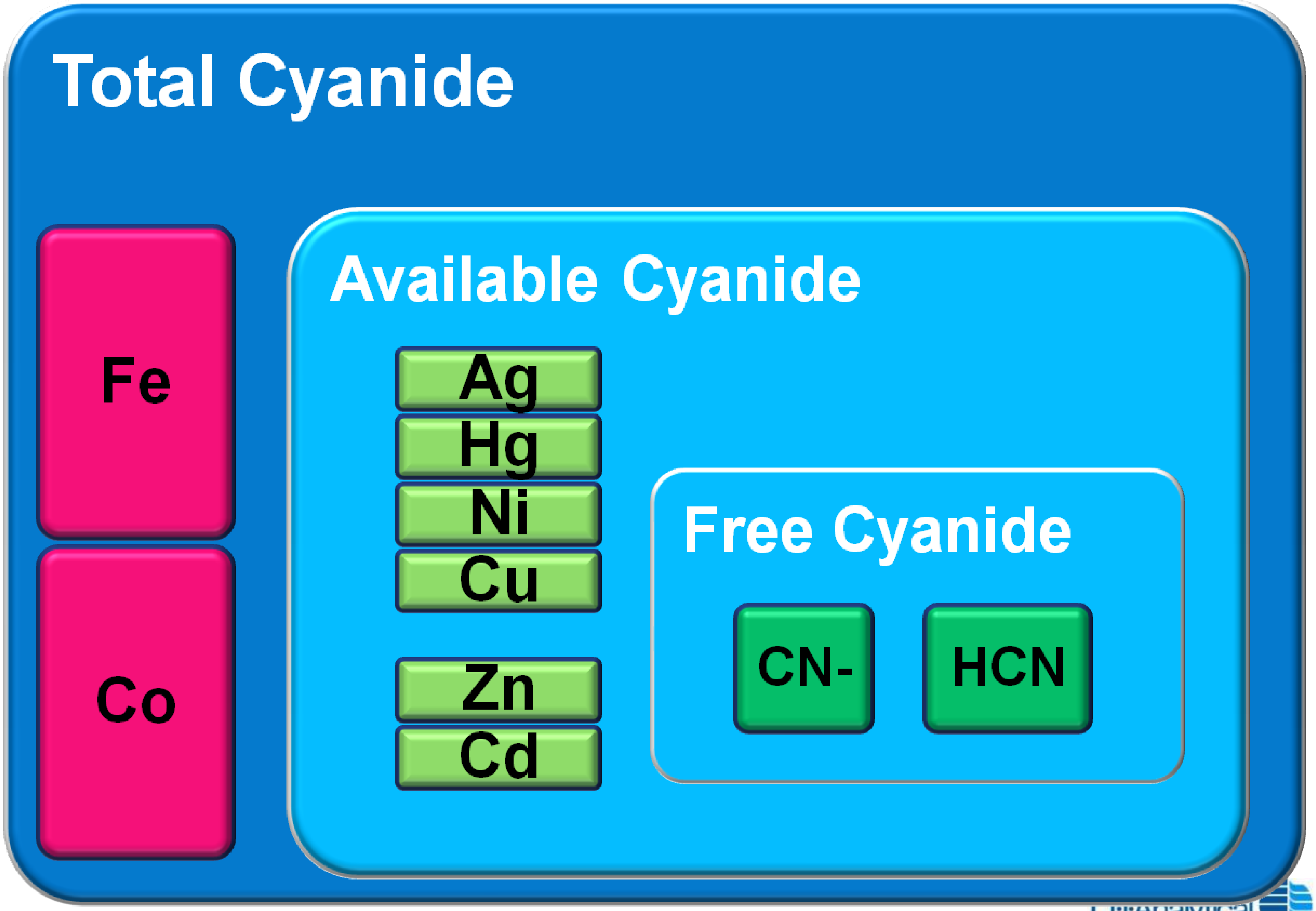
Iron Cyanide Complexes are very stable in the environment

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

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



Cyanide methods measure the various cyanide "species"



Sampling and Sample Preservation

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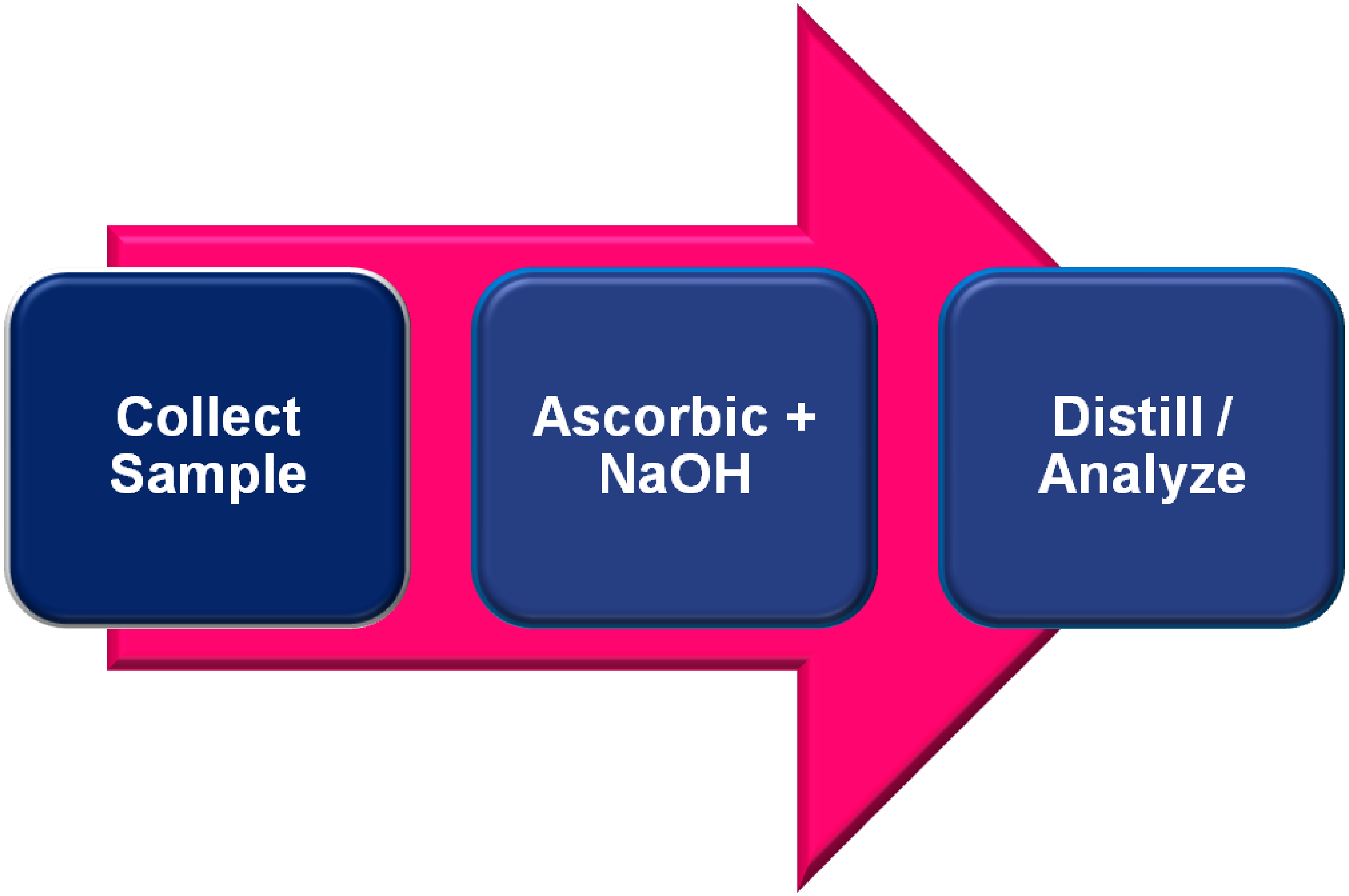
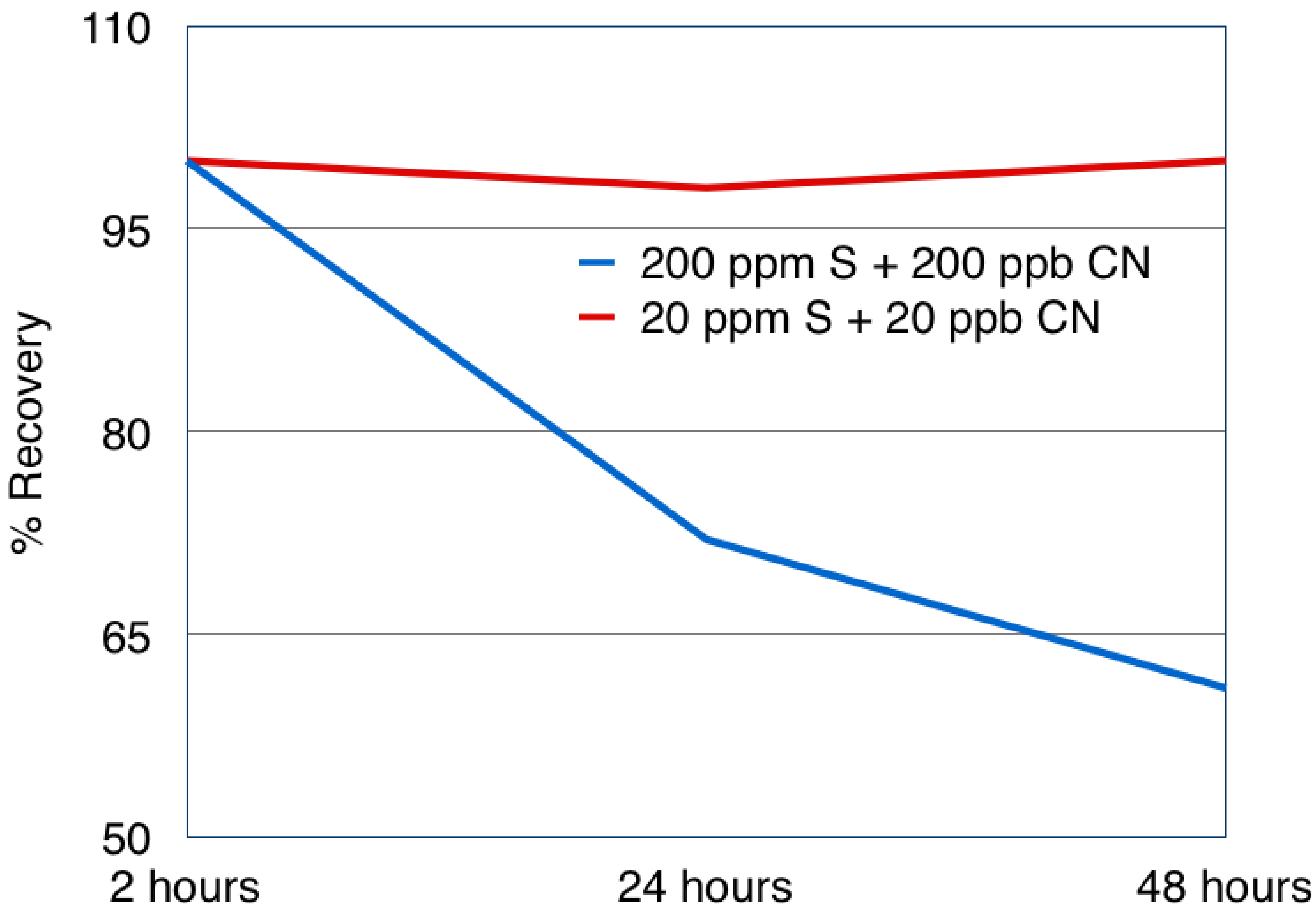
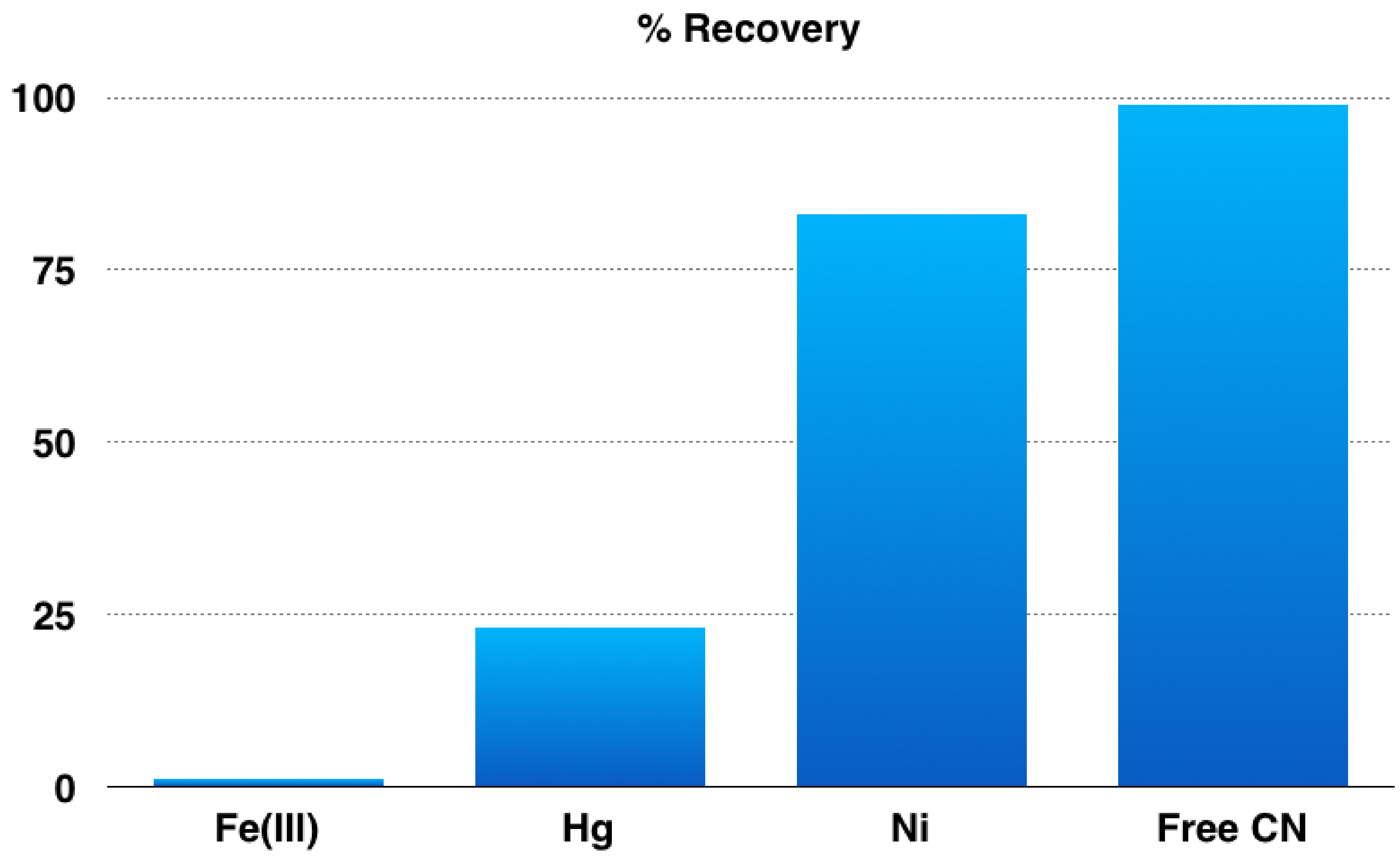

Collect Sample
Ascorbic + NaOH
Distill / Analyze

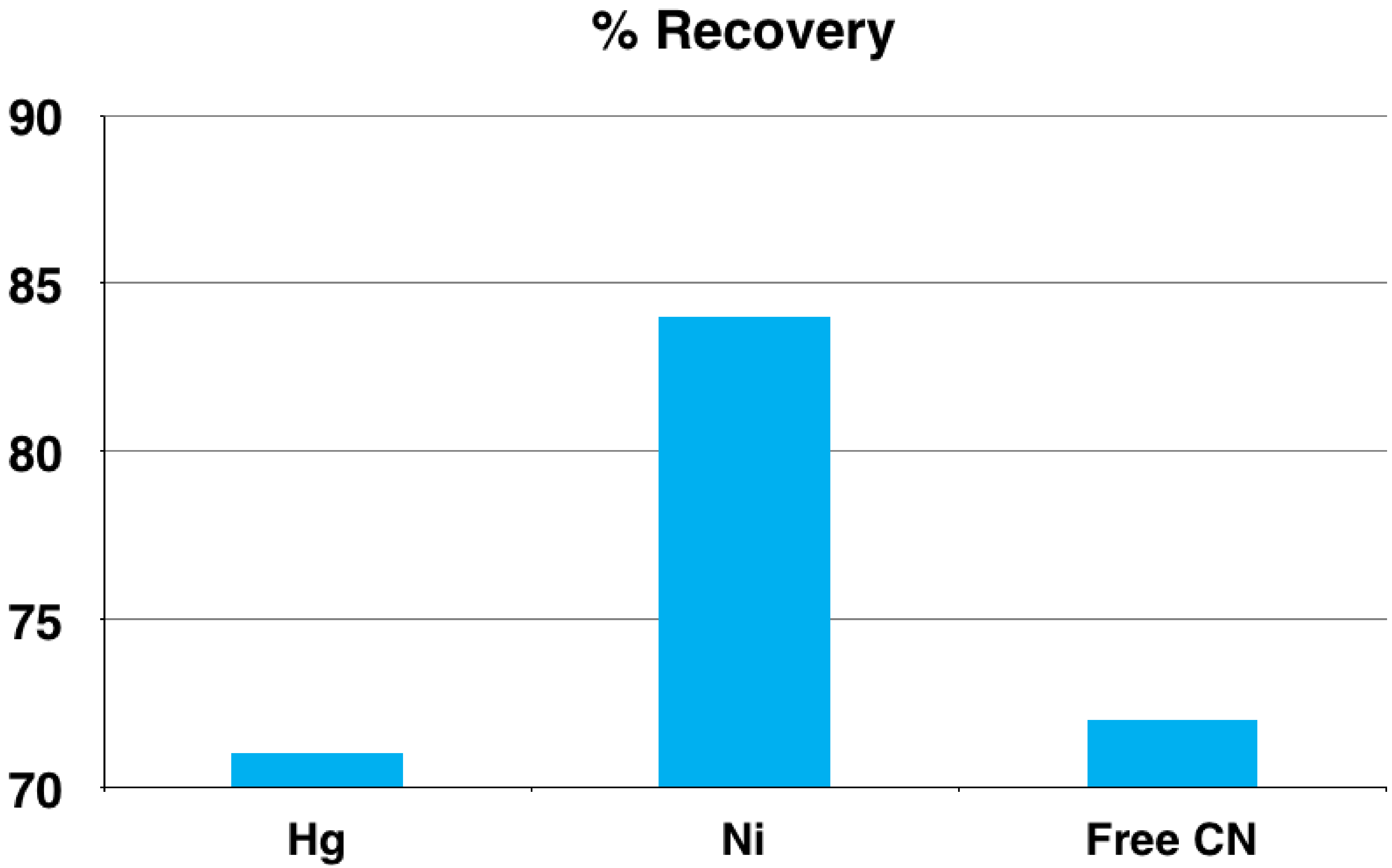
Holding Time Study – Sulfide Bearing Samples



Cannot use Cadmium to Treat Sulfide



Headspace to Treat Sulfide



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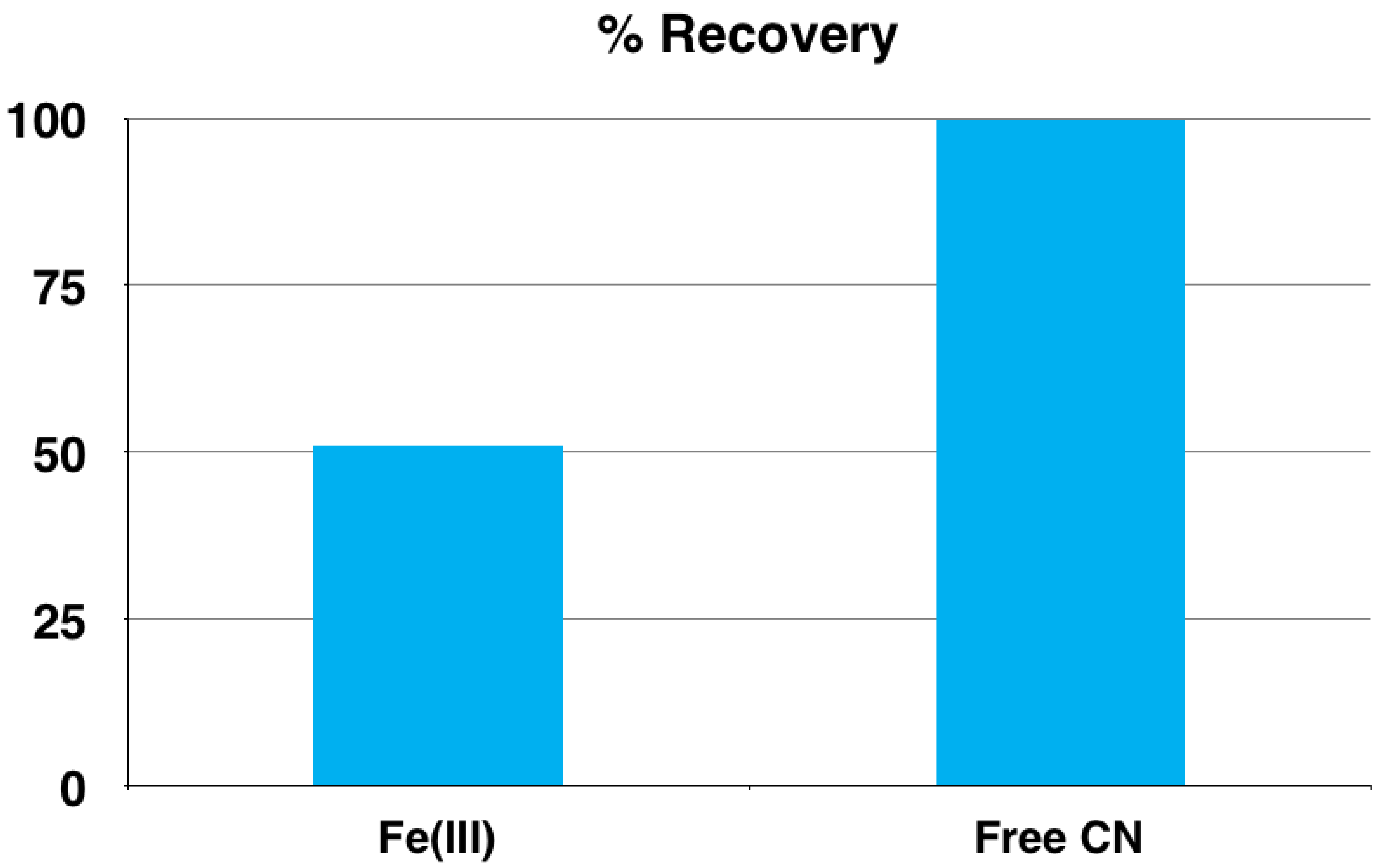
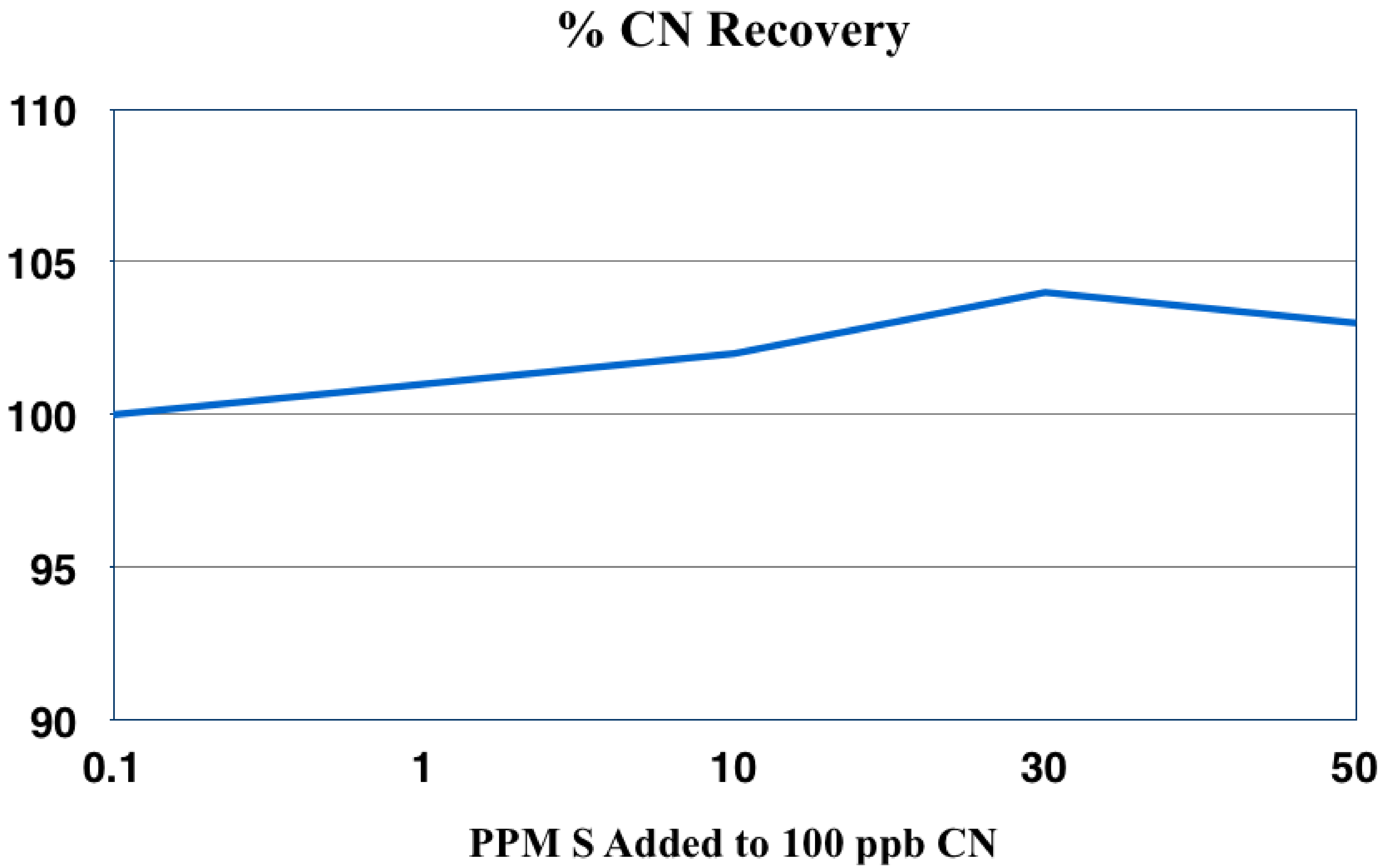
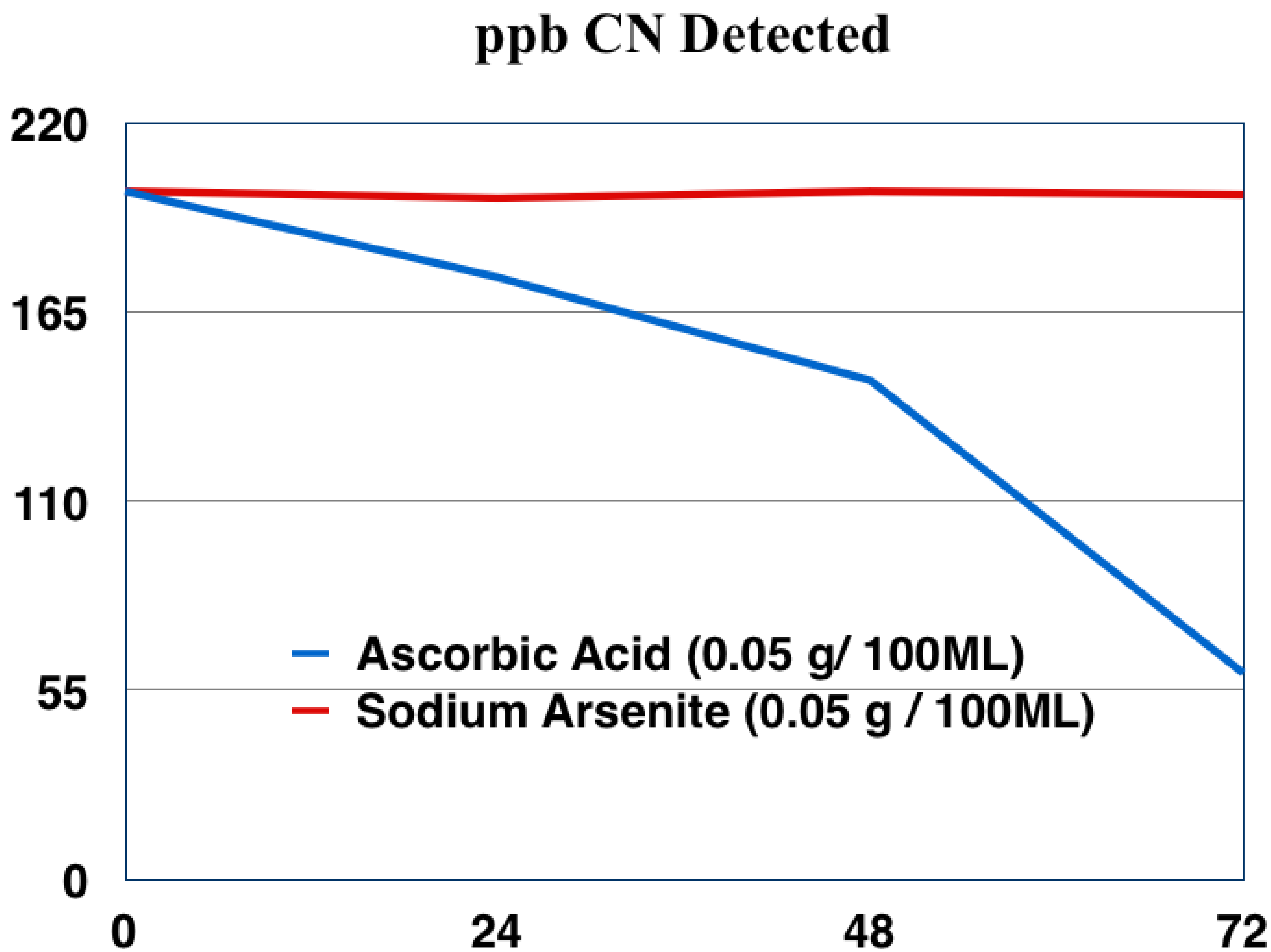
Bismuth to Treat Sulfide then distillation



On-line Sulfide Abatement - ASTM



Oxidizer Removal



Methods and Interferences

Manual "distillation" is used to dissociate as HCN

Macro Distillation

MIDI
Distillations

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Distillation can be automated on a continuous flow analyzer

Distillation and condenser

Distillate

Cyanide methods that utilize distillation have significant disadvantages

Many cyanide interferences result from distillation

- Destroy CN
- Create CN

- UV distillation colorimetry - worst

These compounds are in almost every sample and interfere significantly

Interferences

- Thiocyanate
- Sulfur and Sulfide
- Sulfur (IV) oxides
- Oxidizers

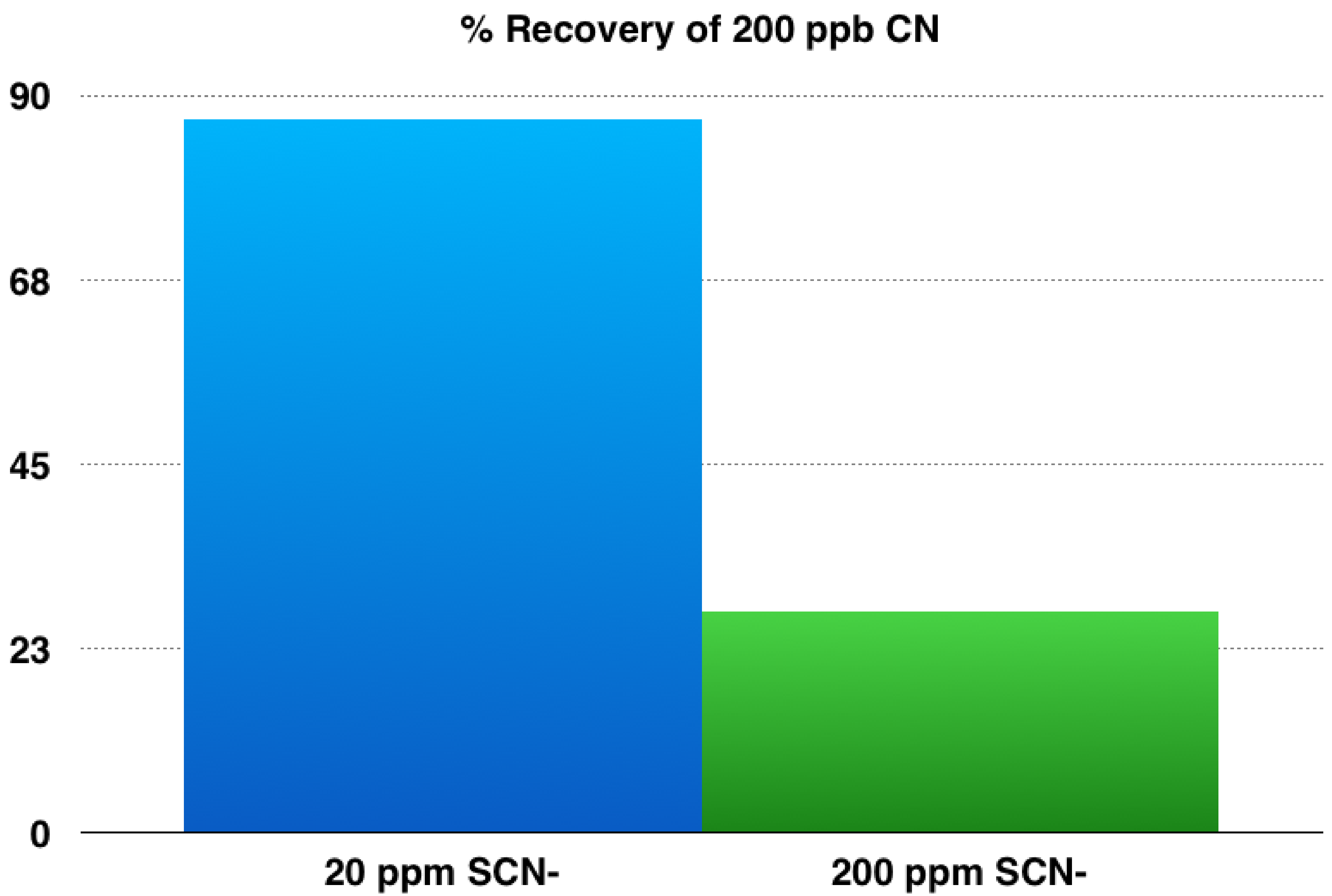
Interferences –

Thiocyanate

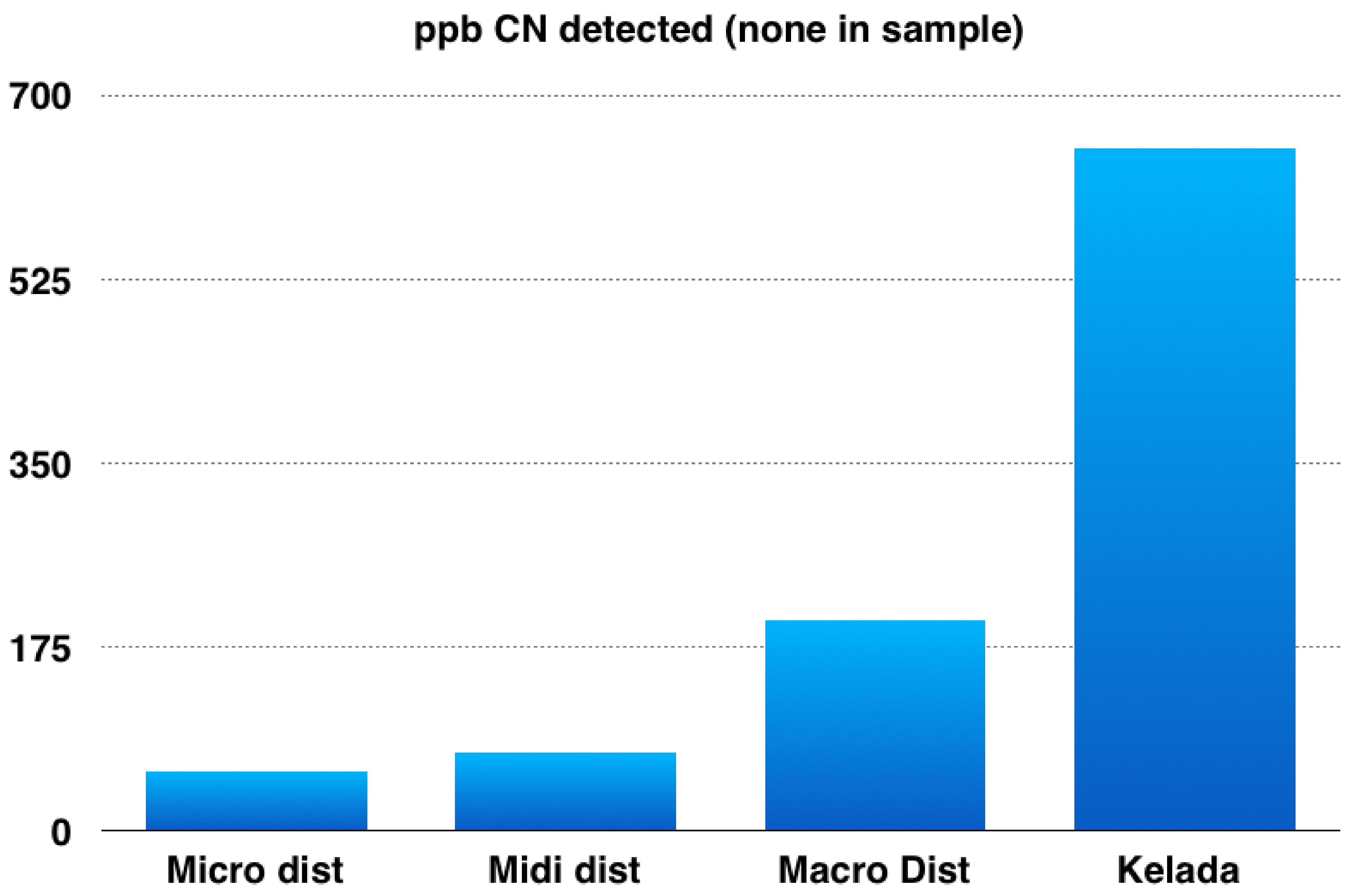
Destroy CN

Create CN

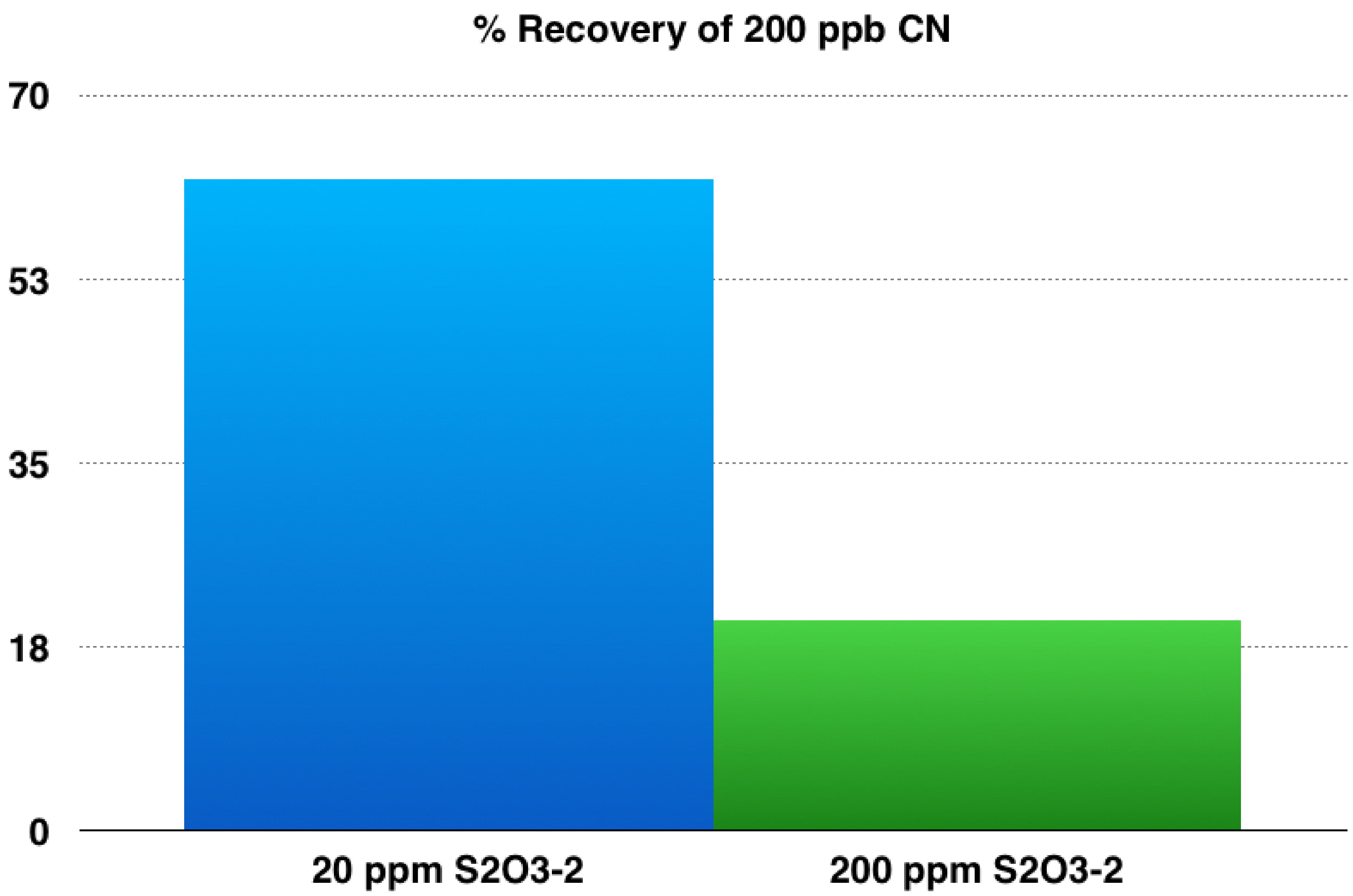
Interferences – Thiocyanate



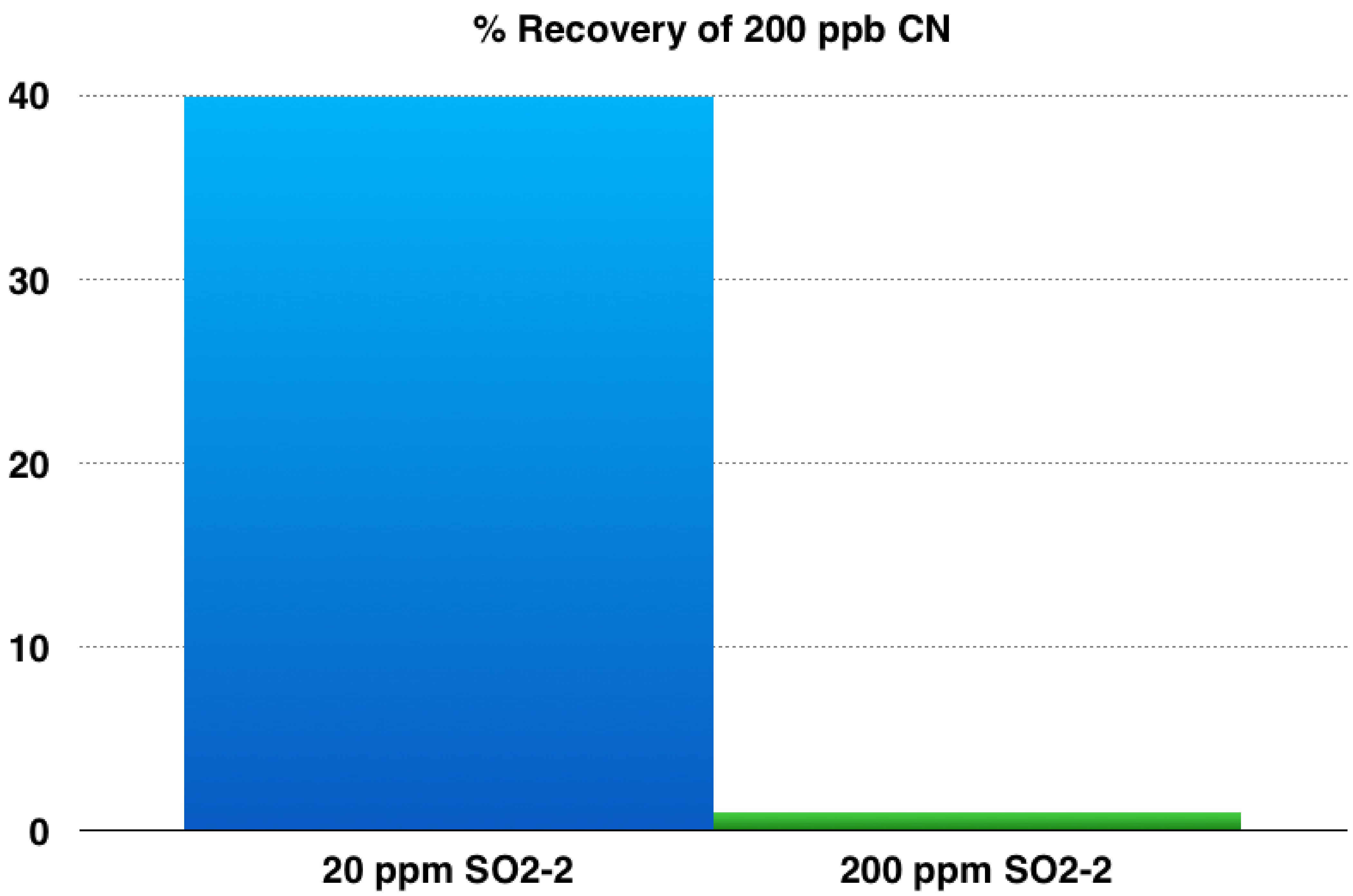
Interferences – Thiocyanate and Nitrate



Interferences – Thiosulfate



Interferences – Sulfite

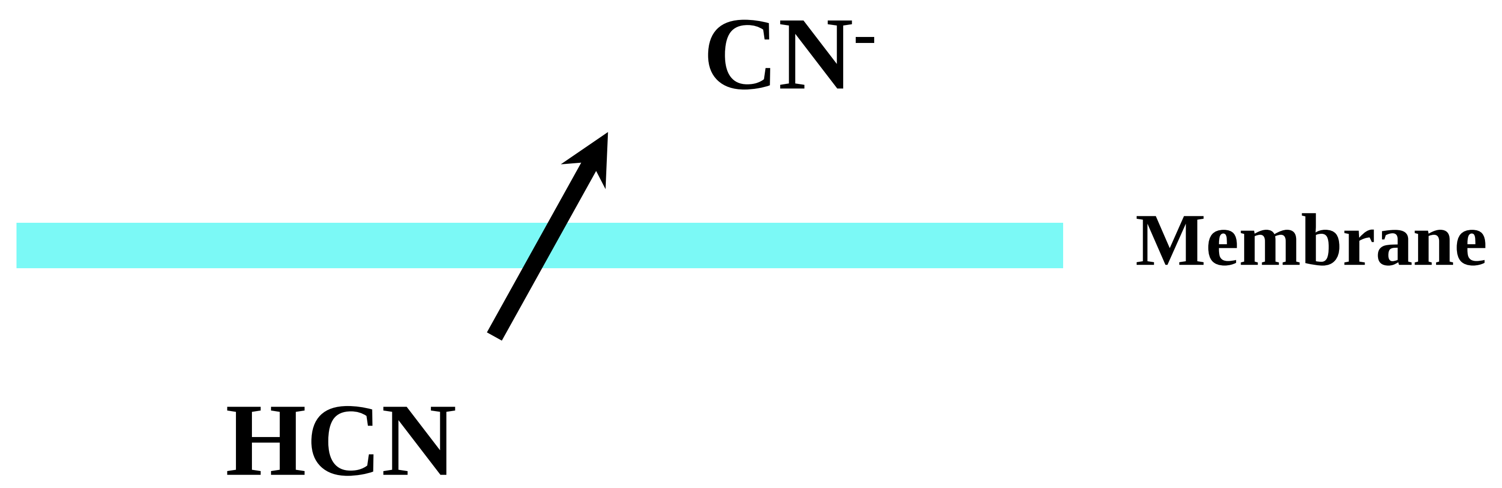


Interferences – Sulfur Compounds

- **No Spot Tests**
- **Dechlorination**

How do you solve interference problems caused by distillation?

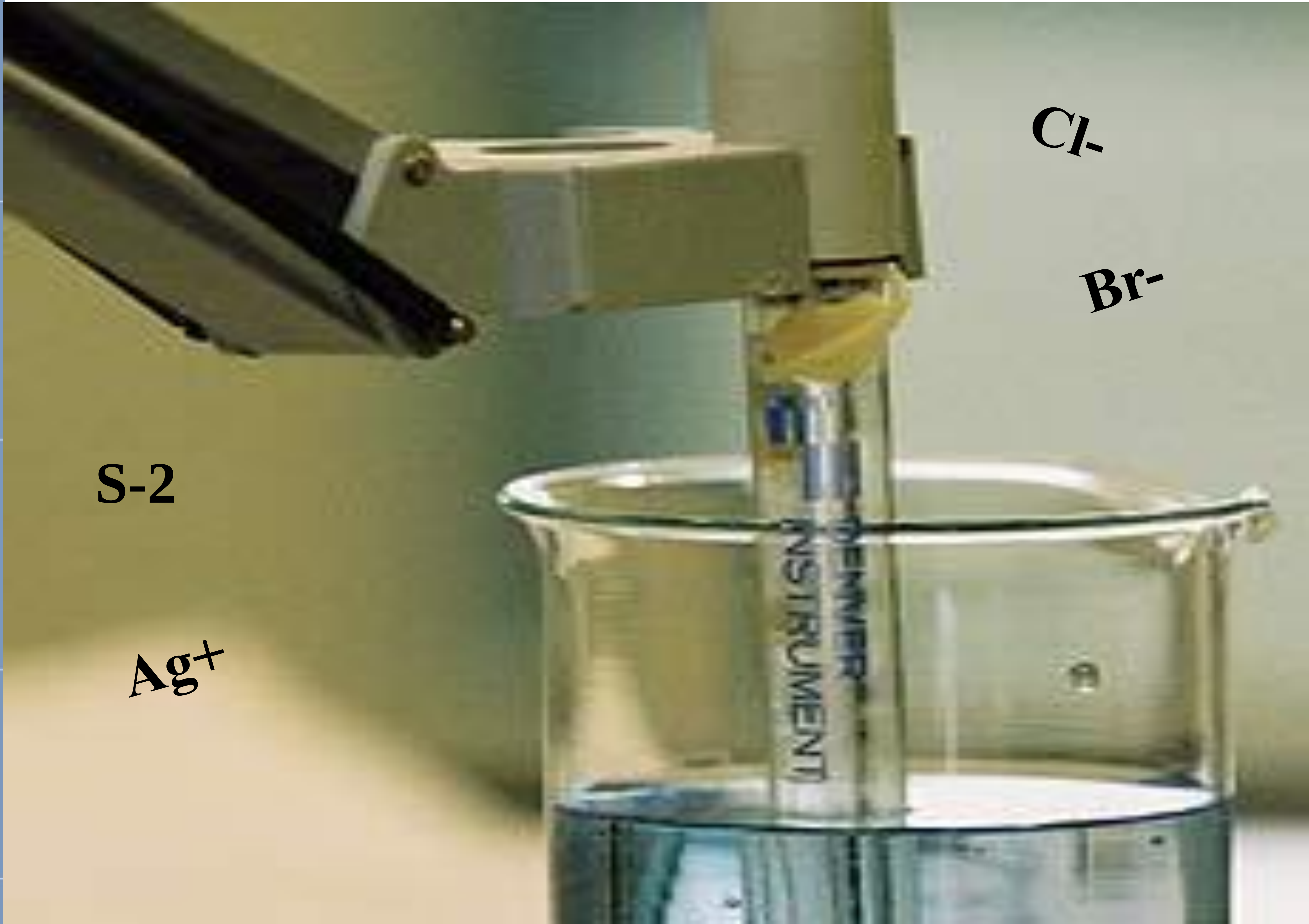
Replace distillation with gas diffusion



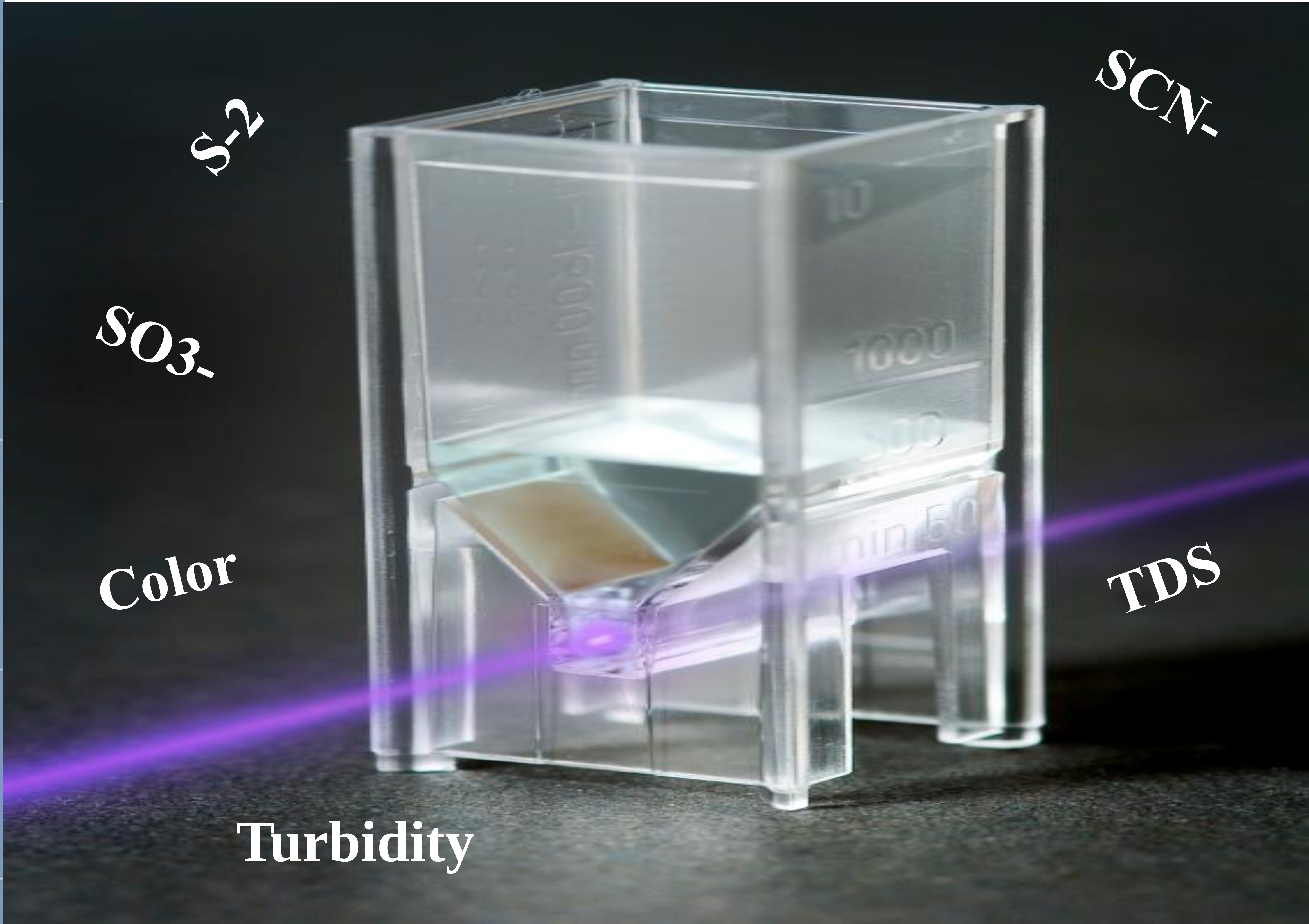
Interferences with Determinative Step

Titration by silver ion

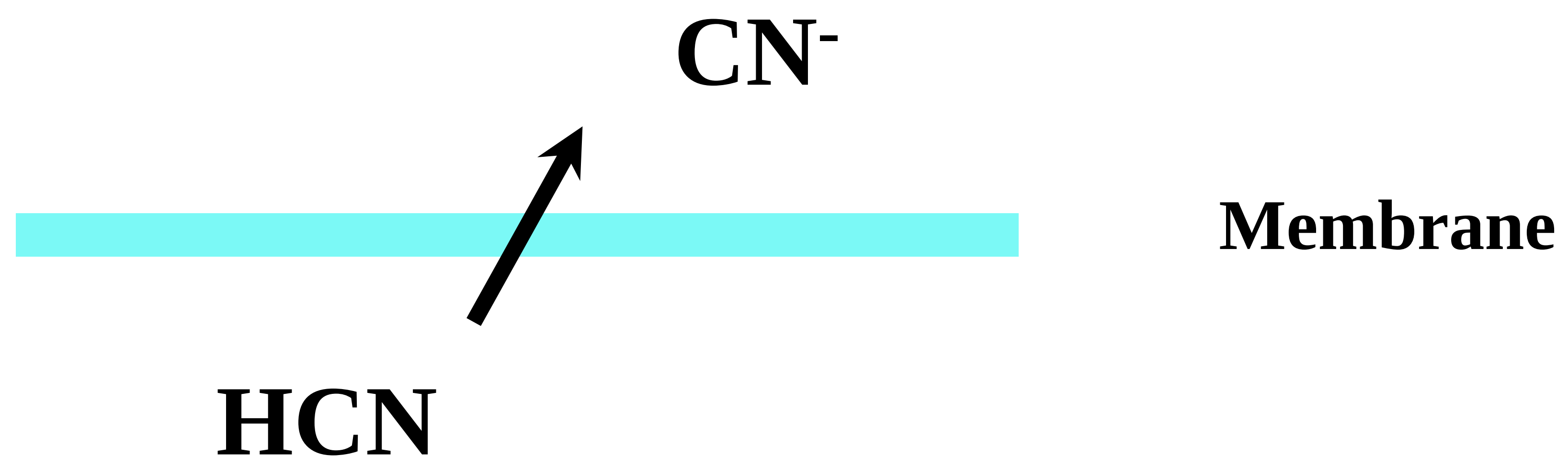
Ion Selective Electrode (ISE)



Colorimetric methods



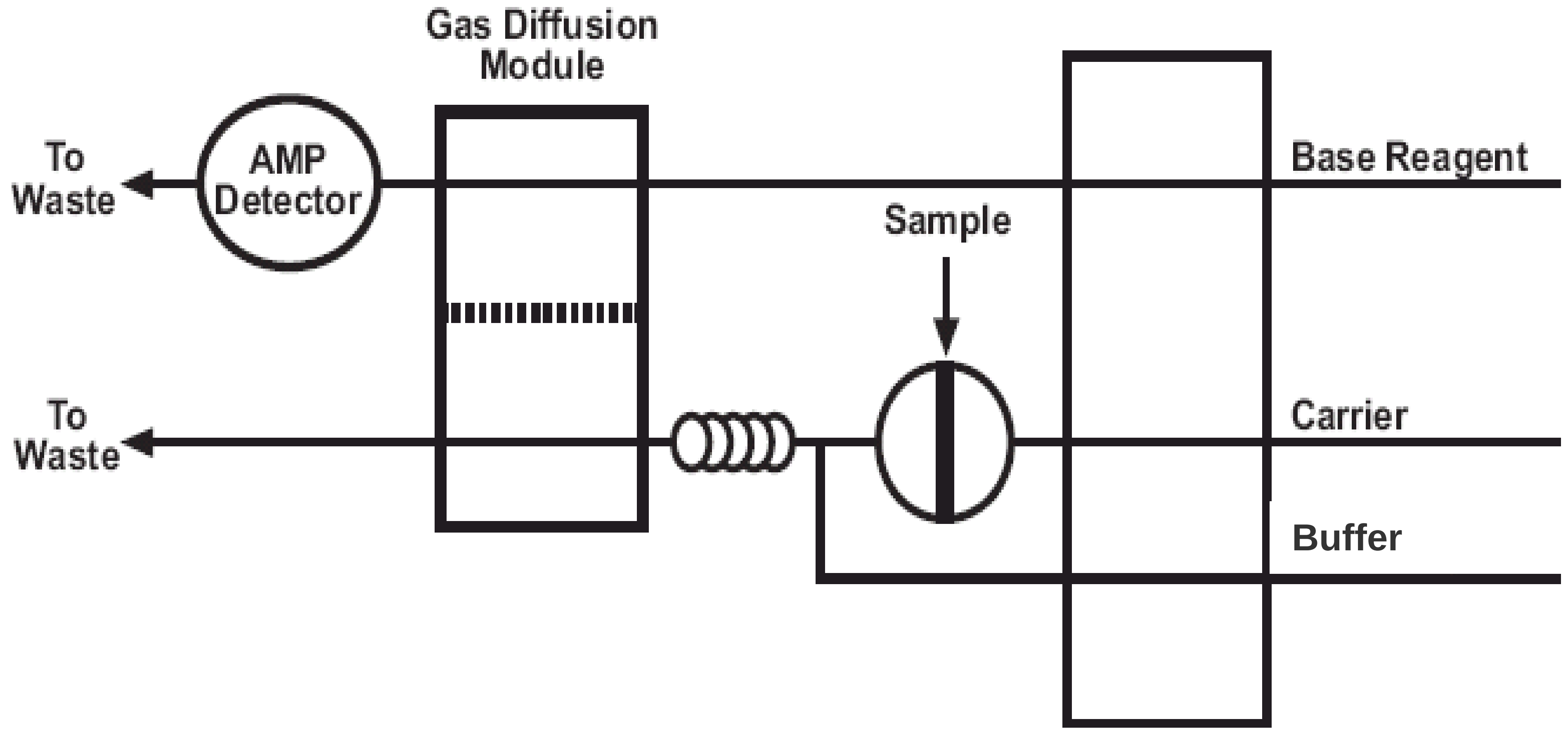
Gas diffusion - Amperometry



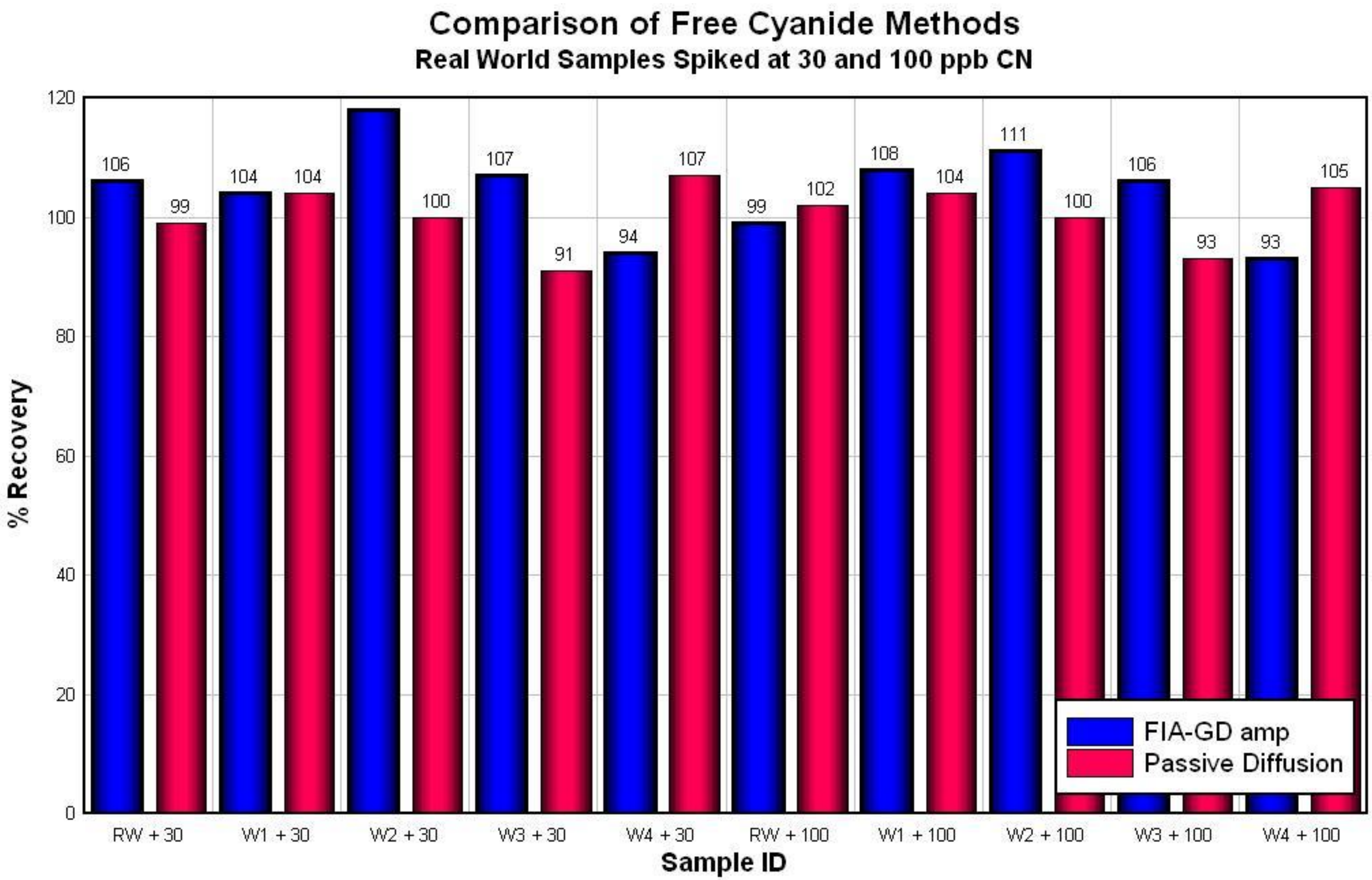
Sulfide > 50 ppm

Free Cyanide Analysis

ASTM D7237-06



Obtain accurate, cost effective free cyanide results in minutes, not hours



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Available Cyanide Analysis

Amenable Cyanide—CATC methods measure "available cyanide"

Method Number	Description	Measurement
SM 4500-CN G	Alkaline Chlorination/ Manual Distillation	Colorimetry
ASTM D 2036	Alkaline Chlorination/ Manual distillation	Colorimetry, Gas Diffusion - Amperometry

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

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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

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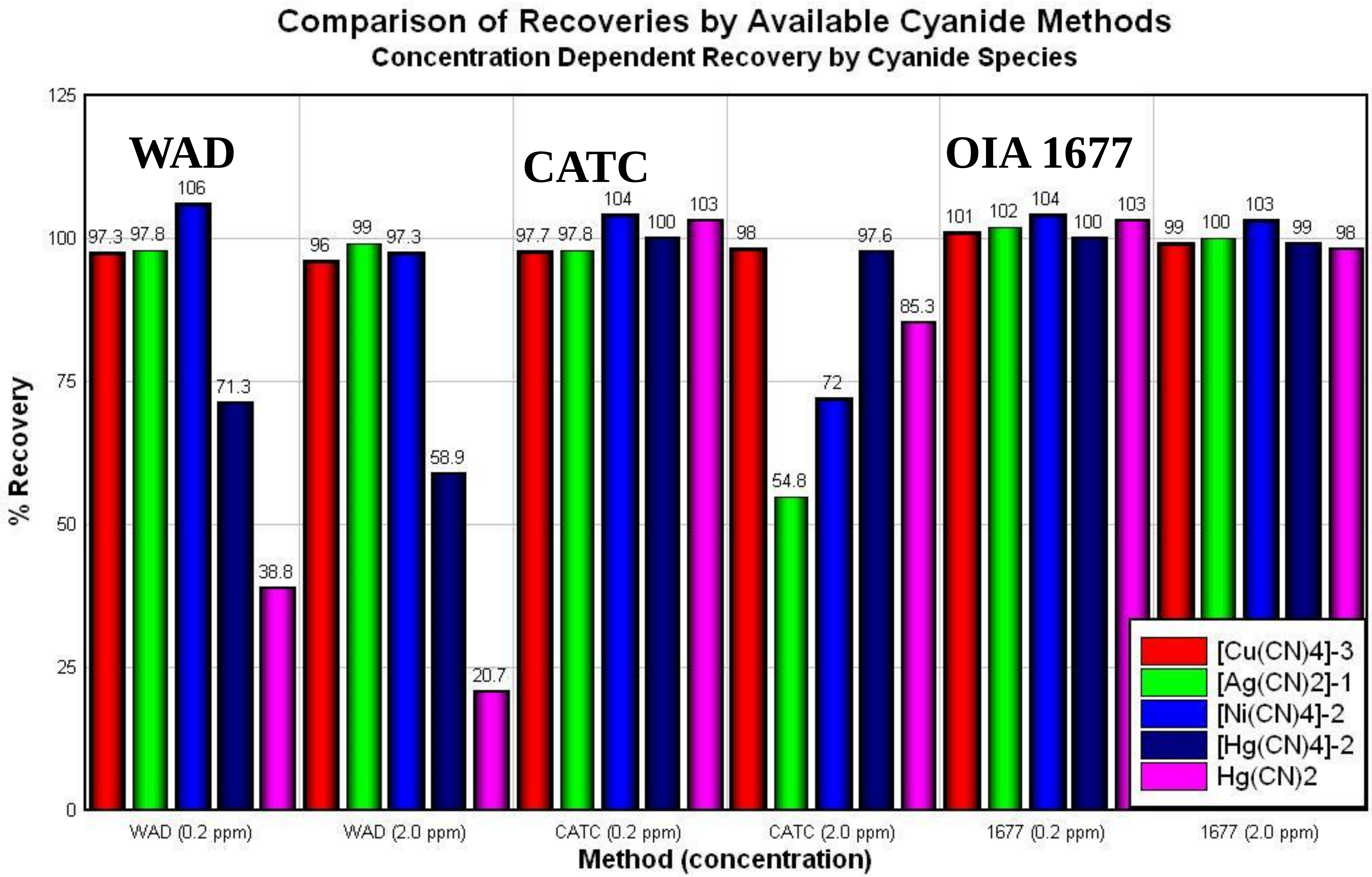
Ligand Exchange GD-amperometry methods get better recovery



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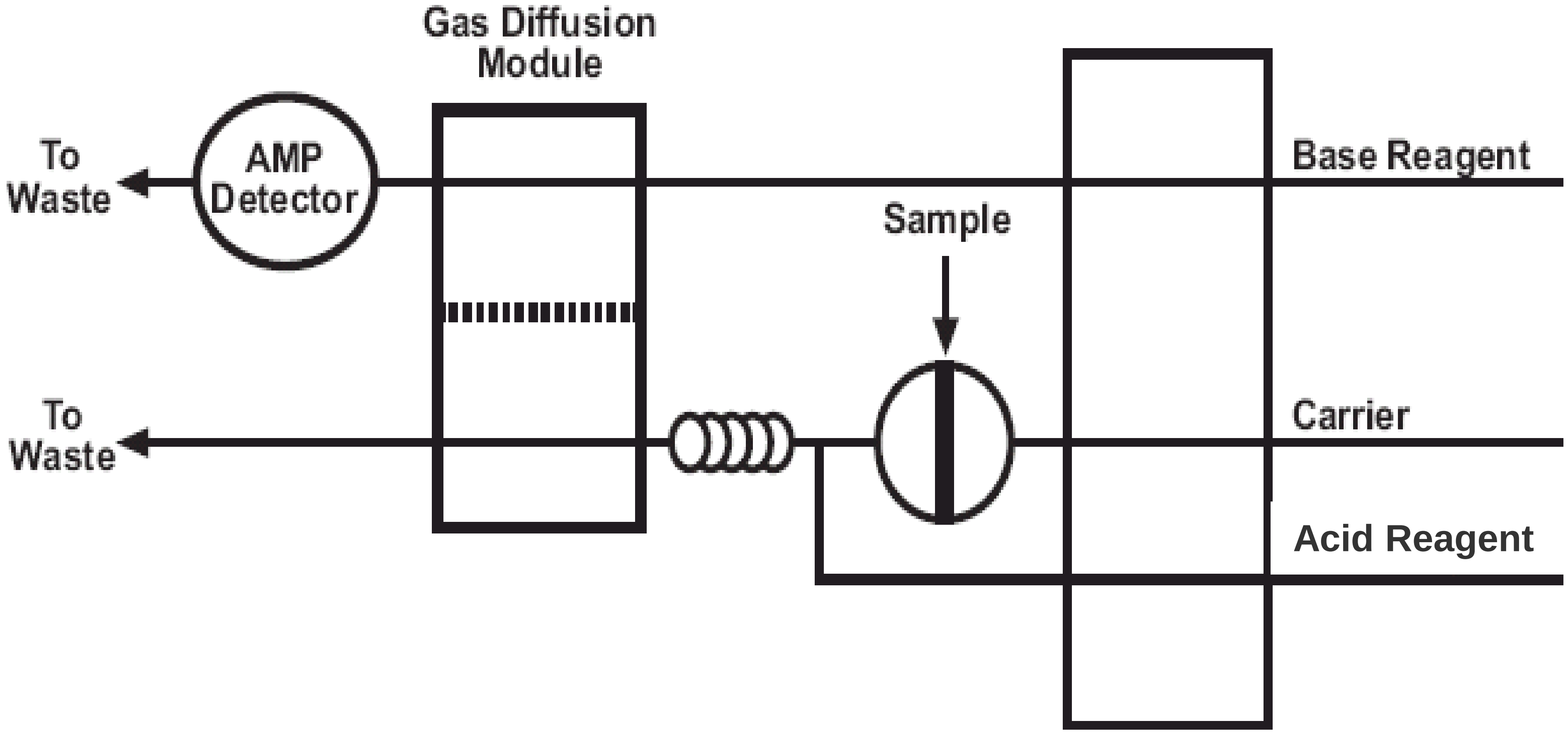
OIA 1677 or ASTM D6888 flow diagram



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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	—	—

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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

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Total Cyanide Analysis

Manual Distillation Methods

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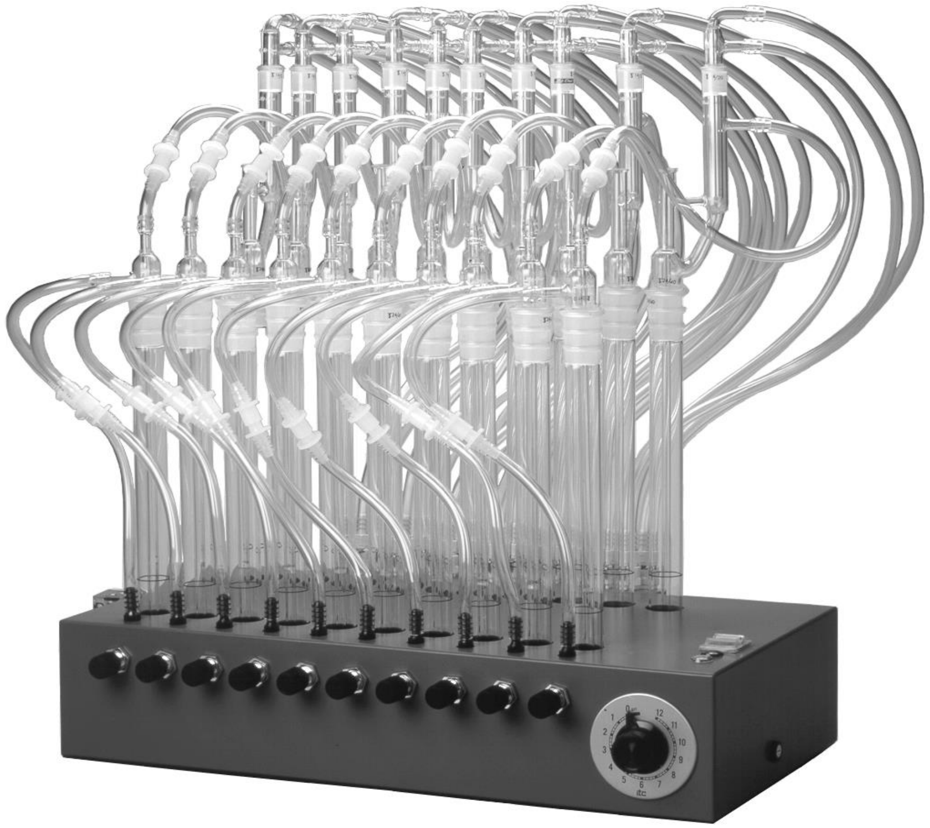
Total cyanide methods using manual distillation

Descriptive Name	Method Number	Description	Measurement
Total Cyanide	EPA 335.4	Midi Distillation – $MgCl_2$	Automated Colorimetry
	ASTM D2036	Midi / Micro/macro Distillation – $MgCl_2$	Colorimetry/ISE/ amperometry/IC
	ASTM D 7284	Midi / Micro Distillation – $MgCl_2$	Gas Diffusion - Amperometry

Most total cyanide analyses are by EPA 335.4 or similar

- Prolonged heating
- strong acid (pH <2)
- Purging into base
- Colorimetry



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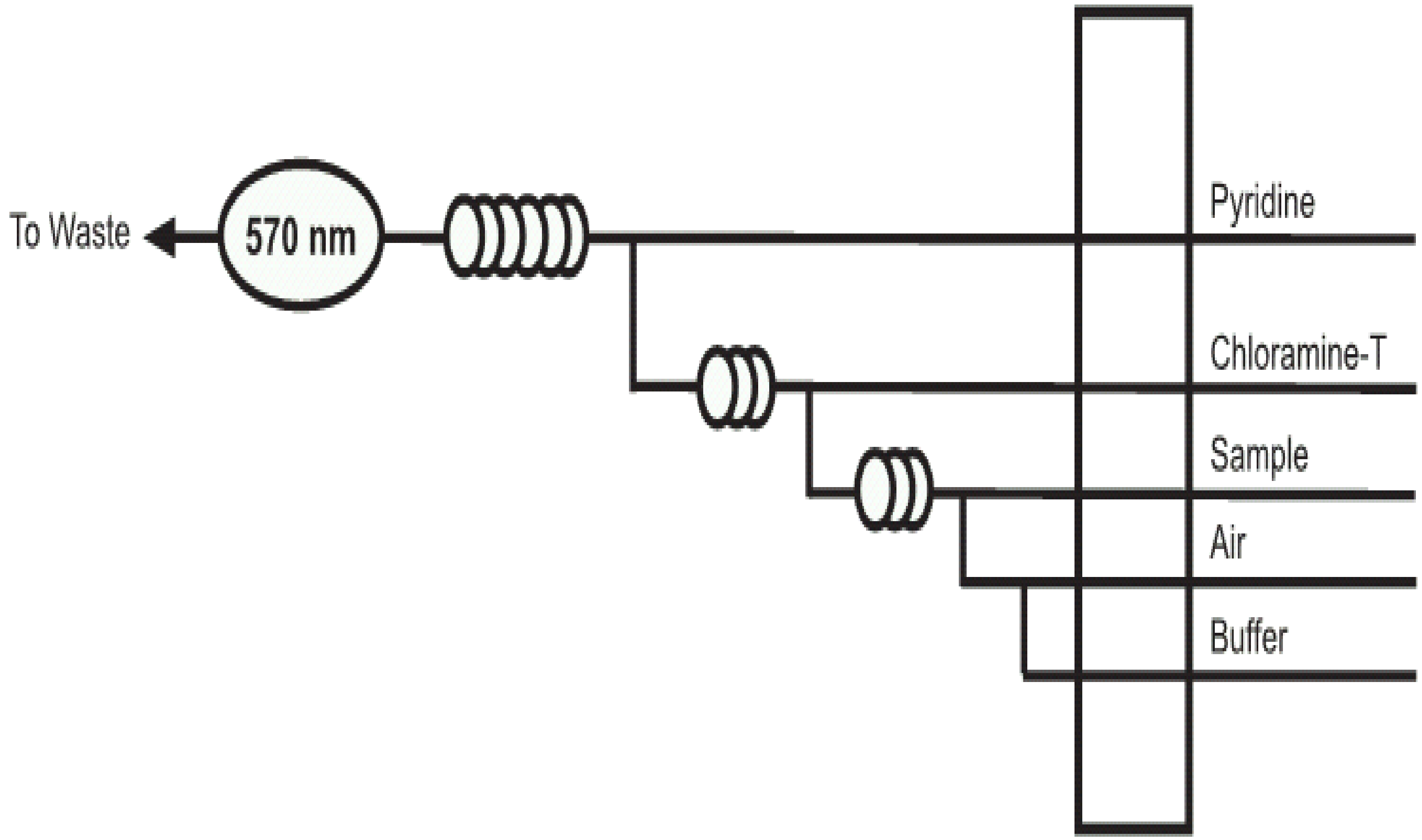
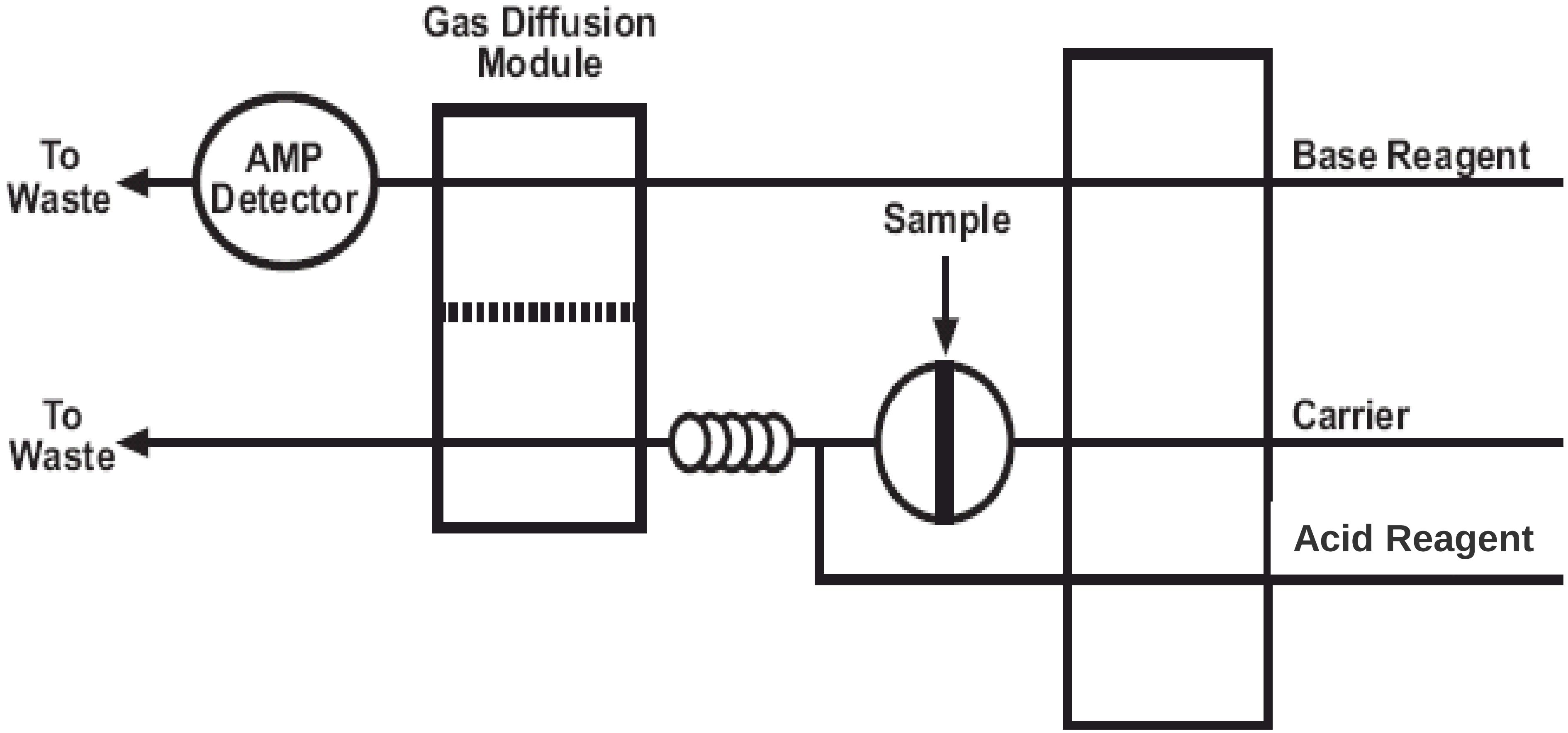
Semi-automated colorimetric cyanide analysis flow diagram



Semi-Automated GD-amperometric by ASTM D7284



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
	ASTM D7511	Low power UV-pH <2	Gas Diffusion - Amperometry

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

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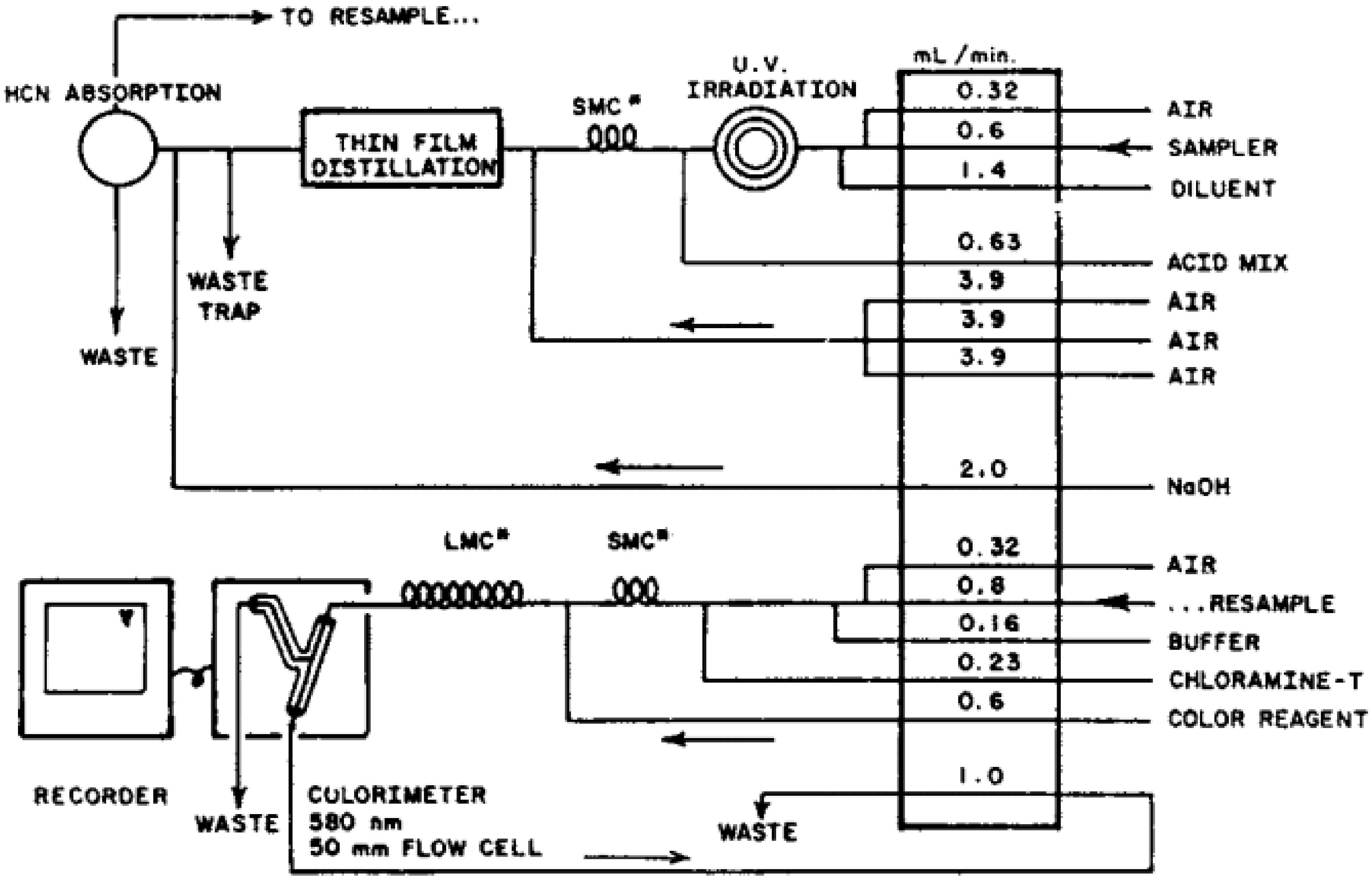
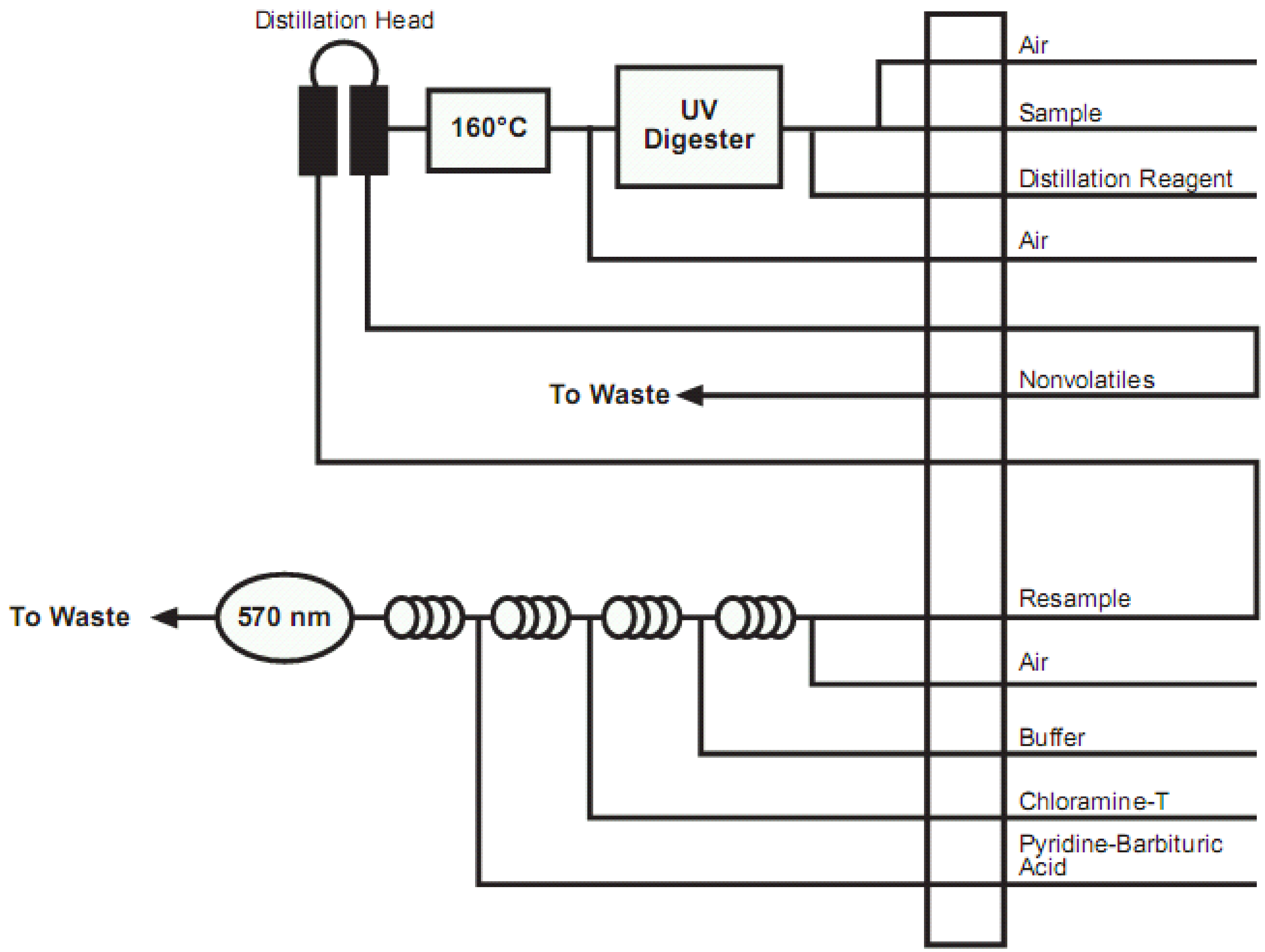
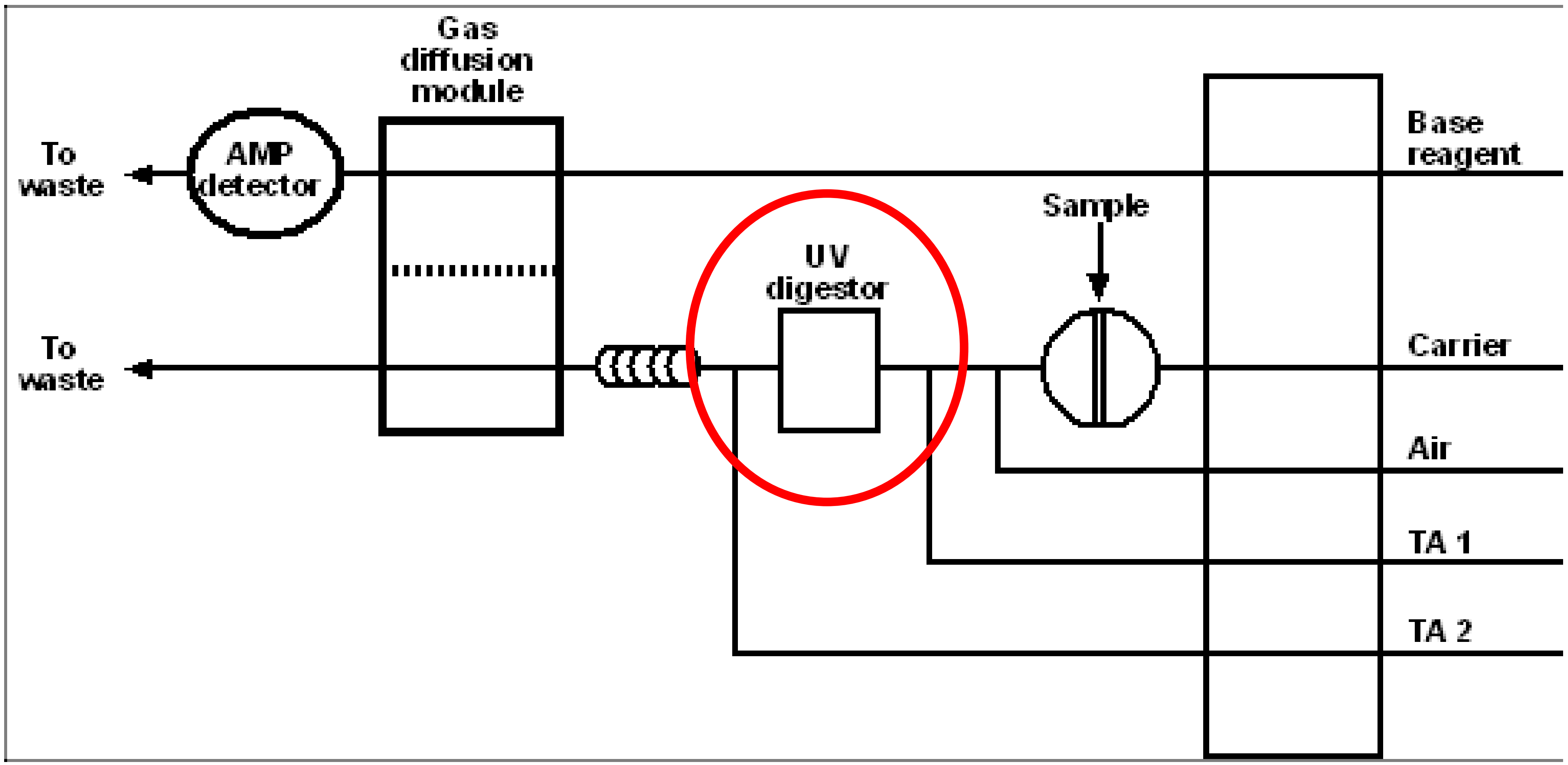
A sample diagram of the Kelada 01 automated cyanide method



A sample diagram of the EPA 335.3 automated cyanide method



A sample diagram of ASTM D7511



Comparison of Kelada and ASTM D7511

	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

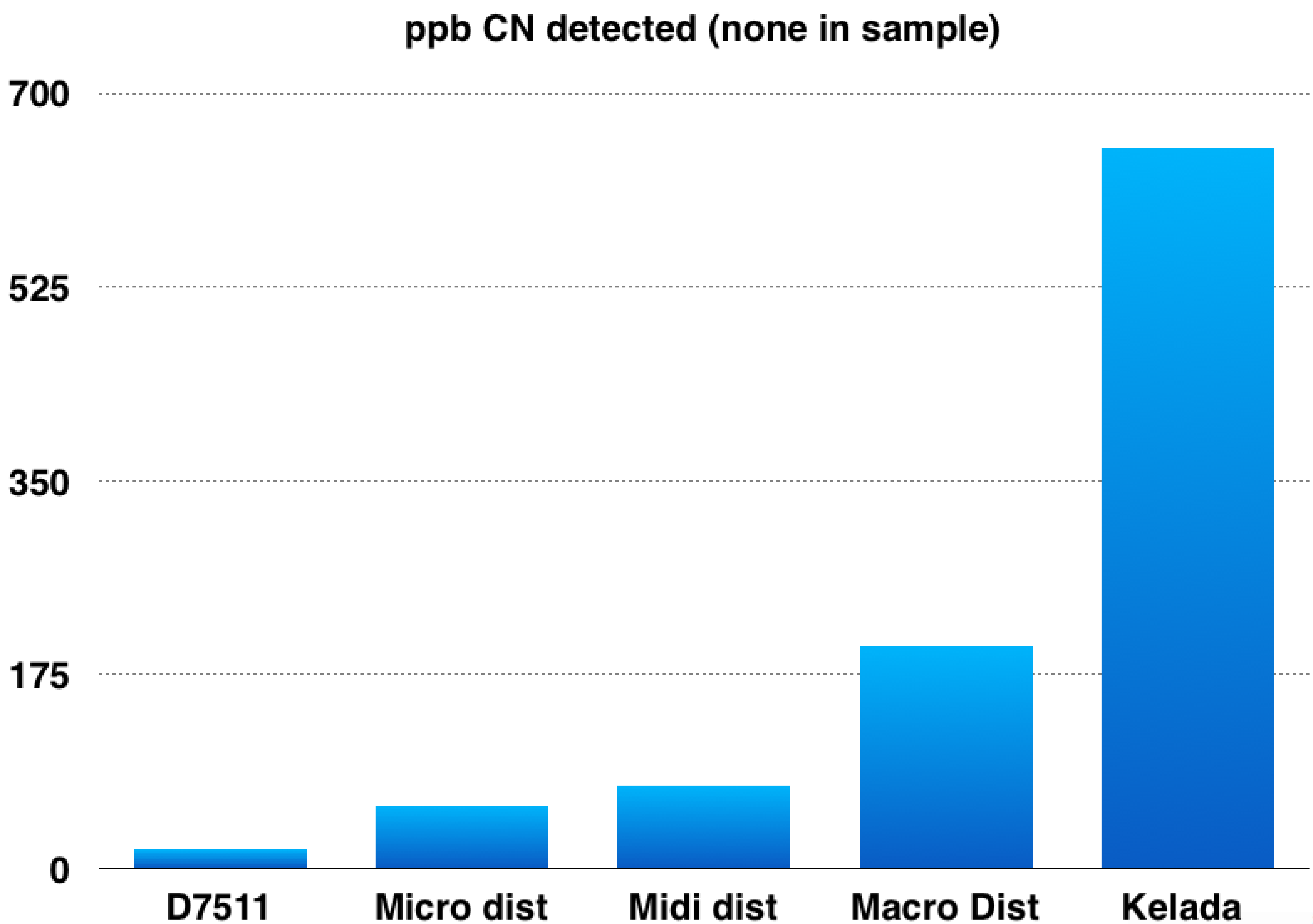
	335.4	ASTM D7284	ASTM D7511
Sample Preparation	2 – 3 hour distillation	1 – 3 hour distillation	No distillation
Analysis	1 – 2 minutes	1 – 2 minutes	1 – 2 minutes
Total Time	3 – 4 hours	2 – 4 hours	1 – 2 minutes

ASTM D7511-09 has fewer interferences than distillation

Interfering Species 20 mg/L	335.4	D7511-09
Nitrite	0.203	0.198
Sulfite	0.08	0.199
Chlorine	0.120	0.118
Thiosulfate	0.124	0.196
Thiocyanate	0.174	0.208
Sulfide	0.120	0.189

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

Interferences – Thiocyanate and Nitrate



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Conclusion

Thank You

Questions?

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