SME 2014

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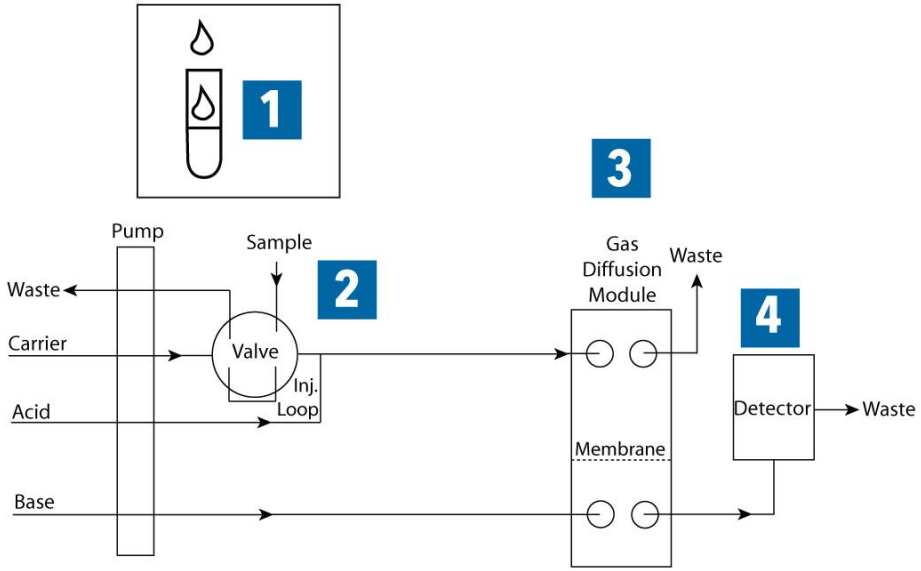
Use of a Flow Injection Gas Diffusion Amperometric Detection On-line Cyanide Analyzer for Control of Cyanide Leaching Solutions

Cyanide Analysis by Gas Diffusion Amperometry

Technique which became U.S. EPA method OIA-1677 for available cyanide was developed in cooperation with University of Nevada-Reno, Mackay School of Mines.[1]

[1] *Rapid Distillationless "Free Cyanide" Determination by a Flow Injection Ligand Exchange Method, Environ. Sci. Technol. Vol. 29, No. 2, 426-430, 1995.*

Available Cyanide Analysis by Gas-Diffusion Amperometry



1 Ligand exchange Pretreatment

$MCN^- + LE \longrightarrow MLE + CN^-$

2 Acidification

$CN^- + H^+ \longrightarrow HCN\ (g)$

3

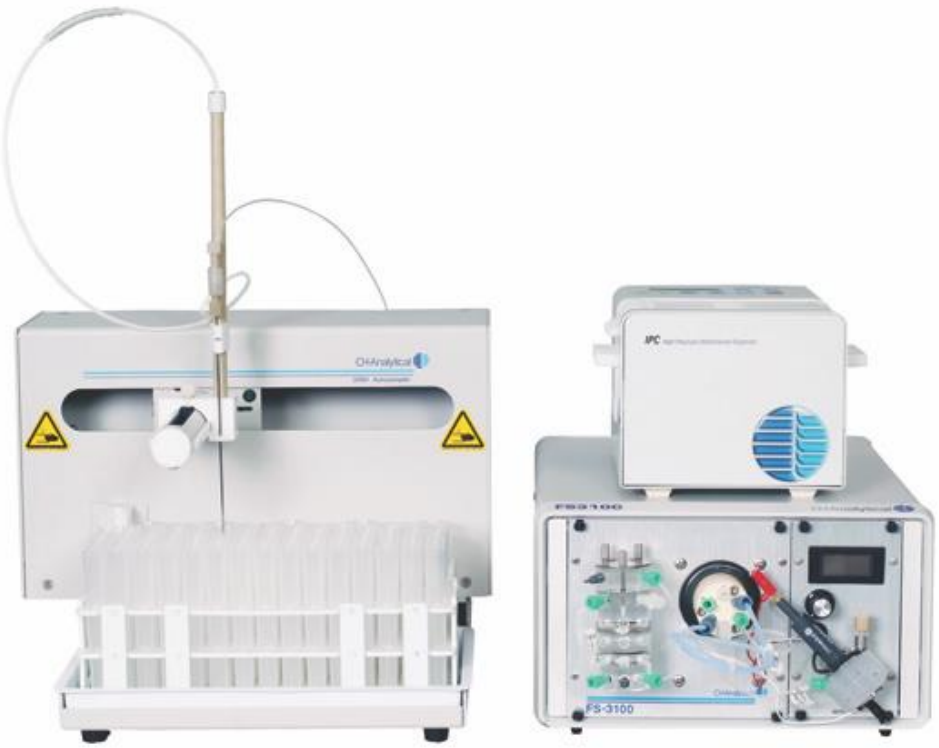
4 Amperometric Detection

$2\ CN^- + Ag \quad Ag(CN)_2^- + e^- \quad$ at + 0.0 V

Gas-Diffusion Amperometry Methods for Available Cyanide Analysis

Method	Application / Use	Regulatory Status
USEPA OIA-1677-09	Drinking Water and Industrial / Municipal Wastewater	USEPA approved for SDWA and NPDES compliance testing/reporting
ASTM D 6888-09	Industrial / Municipal Wastewater	USEPA approved for NPDES compliance testing / reporting
ASTM D 7237-10	Free Cyanide in Industrial / Municipal Wastewater and Effluents	USEPA approved for NPDES compliance testing / reporting
ASTM D 7728-11	WAD Cyanide in Process Solutions Treated Discharges to Surface Water	International Cyanide Management Code Compliance

Lab Analysis by OIA-1677 Method is Used Worldwide for Detox and Leaching Solutions



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Locations Where CNSolution 3100 Lab Analyzers are Used in Gold Mining Operations

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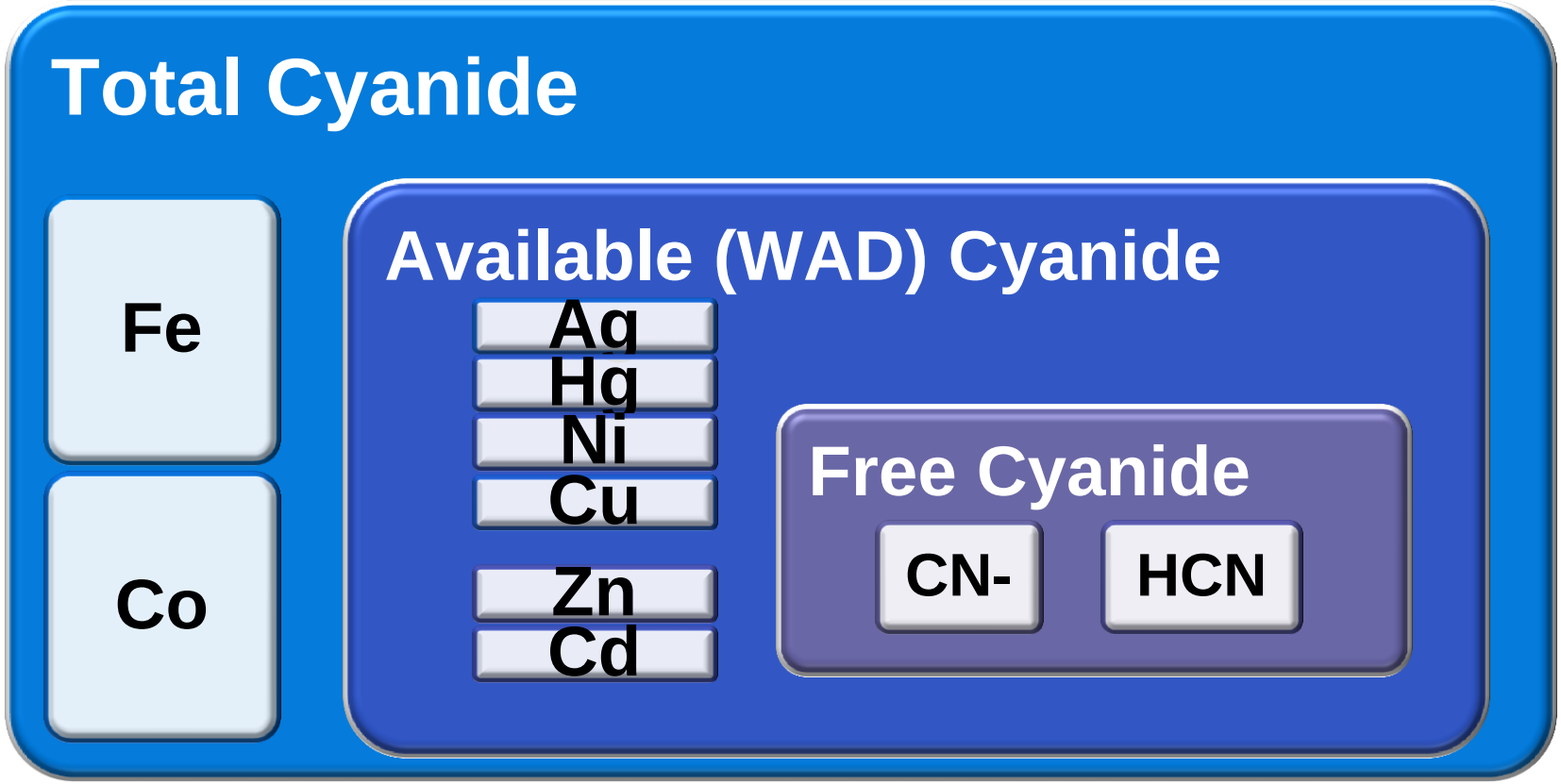
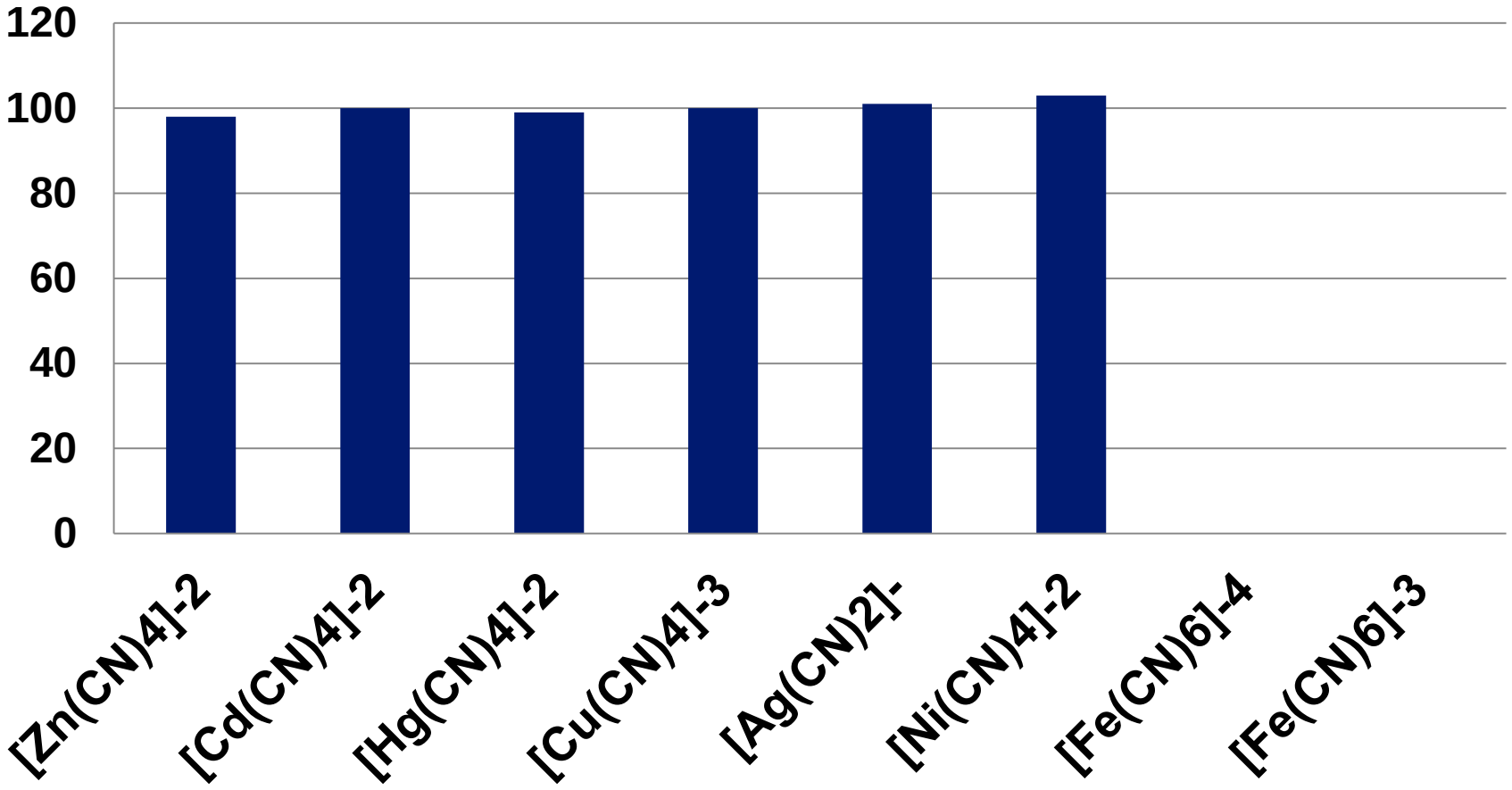
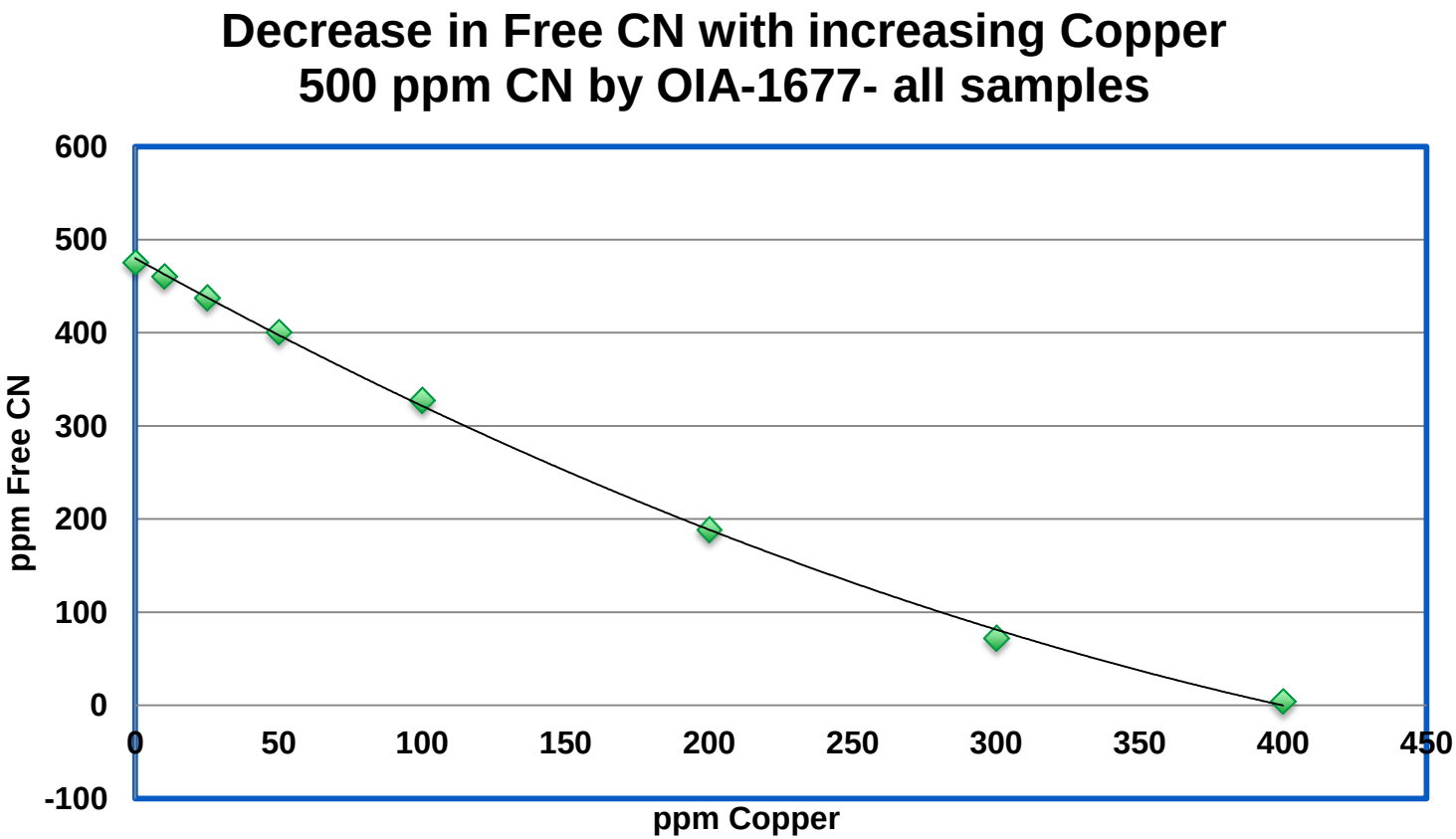
Cyanide Methods Measure Various Cyanide "Species" Dissolved in Water



Recovery of Metal-Cyanide Complexes by OIA-1677



OIA-1677 Recovers all WAD Cyanide in the Leach Solution Including Copper Cyanide



Effect of Copper on Gold Cyanidation

Copper complexes cyanide making it unavailable for leaching

Using OIA-1677 to Measure Free Cyanide in Leaching Solutions

1. Measure cyanide by OIA-1677
2. Determine copper by AA or ICP
3. Measure pH
4. Use “cyanide species calculator”
5. Obtain “actual free cyanide”

Determination of “Free Cyanide” in Leaching Solutions Using OIA-1677

OIA – 1677 CN (ppm)	Copper (ppm)	“actual free CN” (ppm)	Titrated free CN (ppm)
824	236	432	640
1129	602	206	260
1944	1254	111	400
879	177	570	770
987	260	548	720
868	588	53	160

Titration measures some, but not all, of the copper cyanide

Titration overestimates free cyanide

CNSolution 9310 On-line Cyanide Analyzer

Measures available cyanide in precious metal leaching solutions by U.S. EPA Method OIA-1677 and ASTM D 6888-09.

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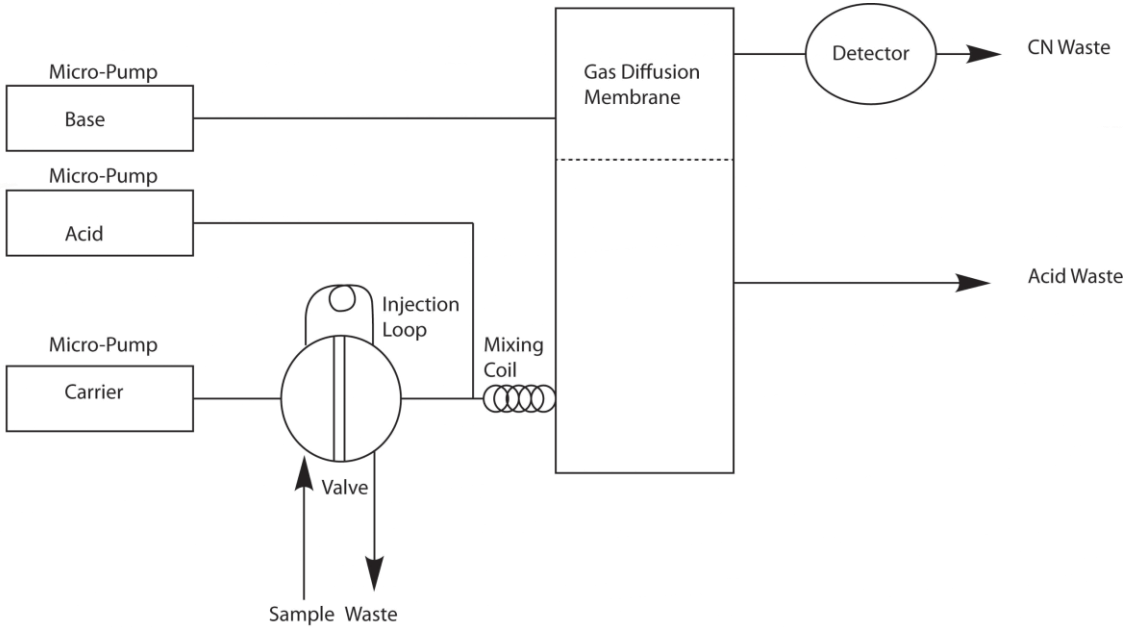
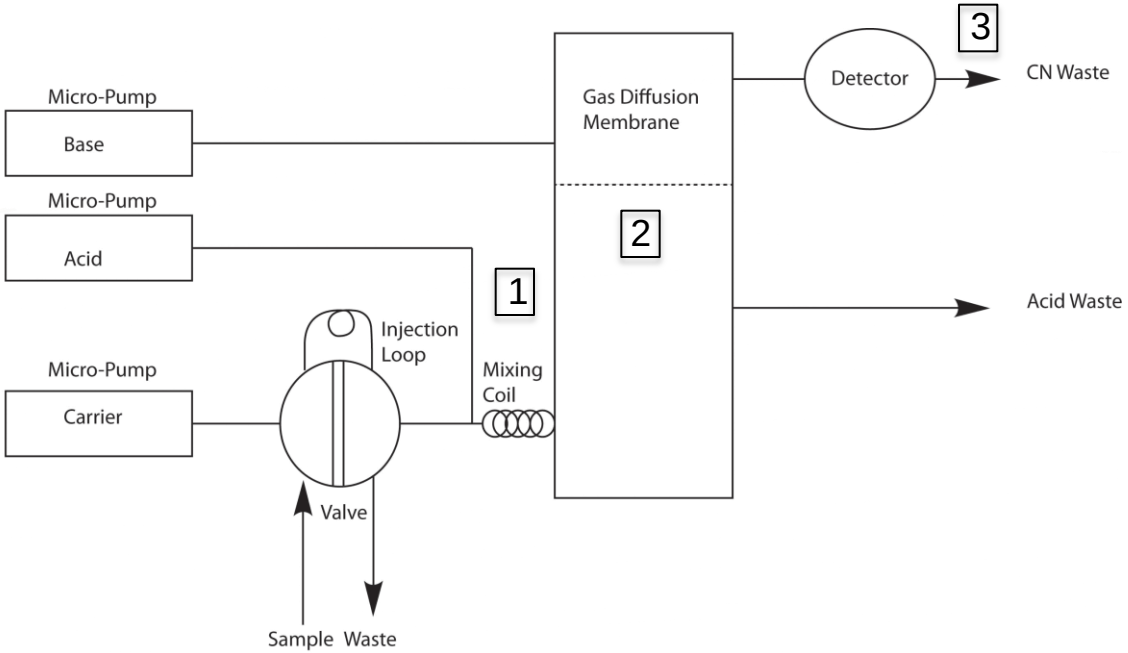
CNSolution 9310 Flow Diagram



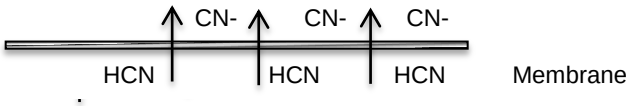
CNSolution 9310 – Available Cyanide Analysis by FIA Gas Diffusion Amperometry



1 Acidification

$CN^- + H^+ \longrightarrow HCN\ (g)$

2 Gas Diffusion



3 Amperometric Detection

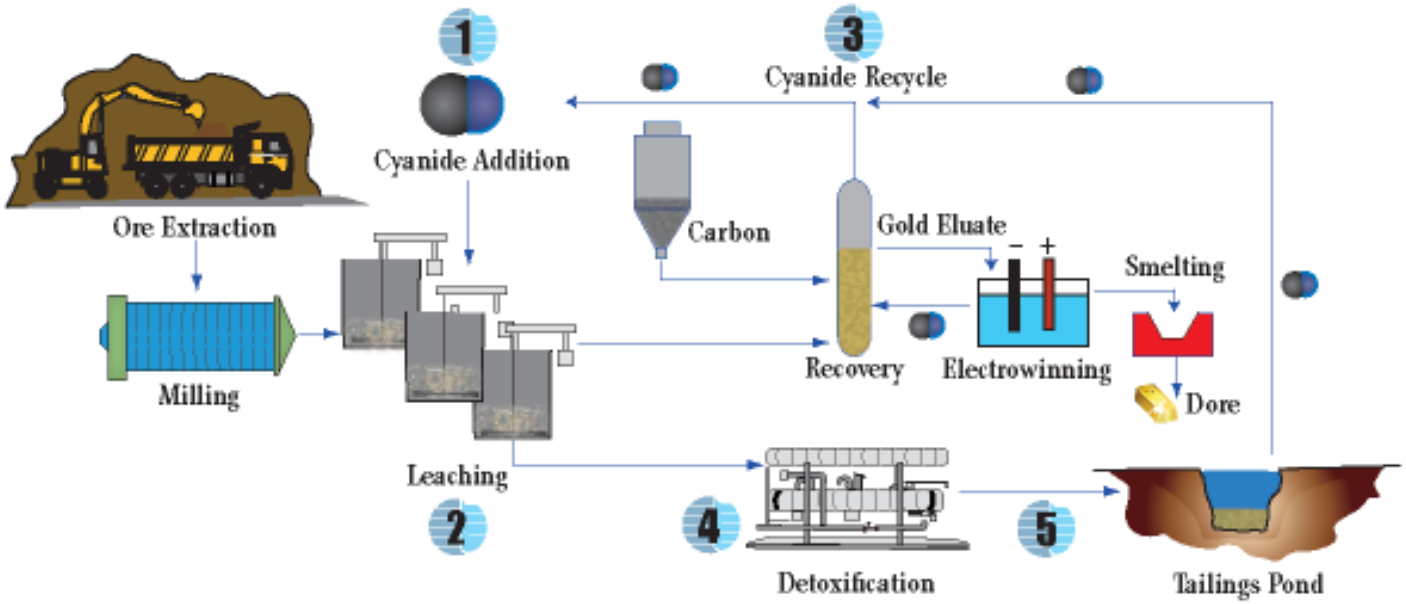
$2\ CN^- + Ag \quad Ag(CN)^-_2 + e^- \quad at + 0.0V$

CNSolution 9310 On-line Cyanide Analyzer

Measurement Ranges

- 0.2 to 50 ppm CN
- 2.0 to 500 ppm CN
- 20 to 2,000 ppm CN

CNSolution 9310 Deployment in Precious Metal Cyanidation



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Accuracy of 5 Different CNSolution 9310 Analyzers

Standard	Instrument 1	Instrument 2	Instrument 3	Instrument 4	Instrument 5
2 ppm	2.17	1.95	2.12	1.95	2.14
5 ppm	5.25	5.04	5.03	4.93	5.40
10 ppm	10.2	10.3	9.50	10.1	10.7
20 ppm	21.5	20.3	19.4	20.5	20.7
50 ppm	50.7	49.5	48.5	49.5	50.5
100 ppm	101	99.6	96	101	104
200 ppm	199	193	198	205	201

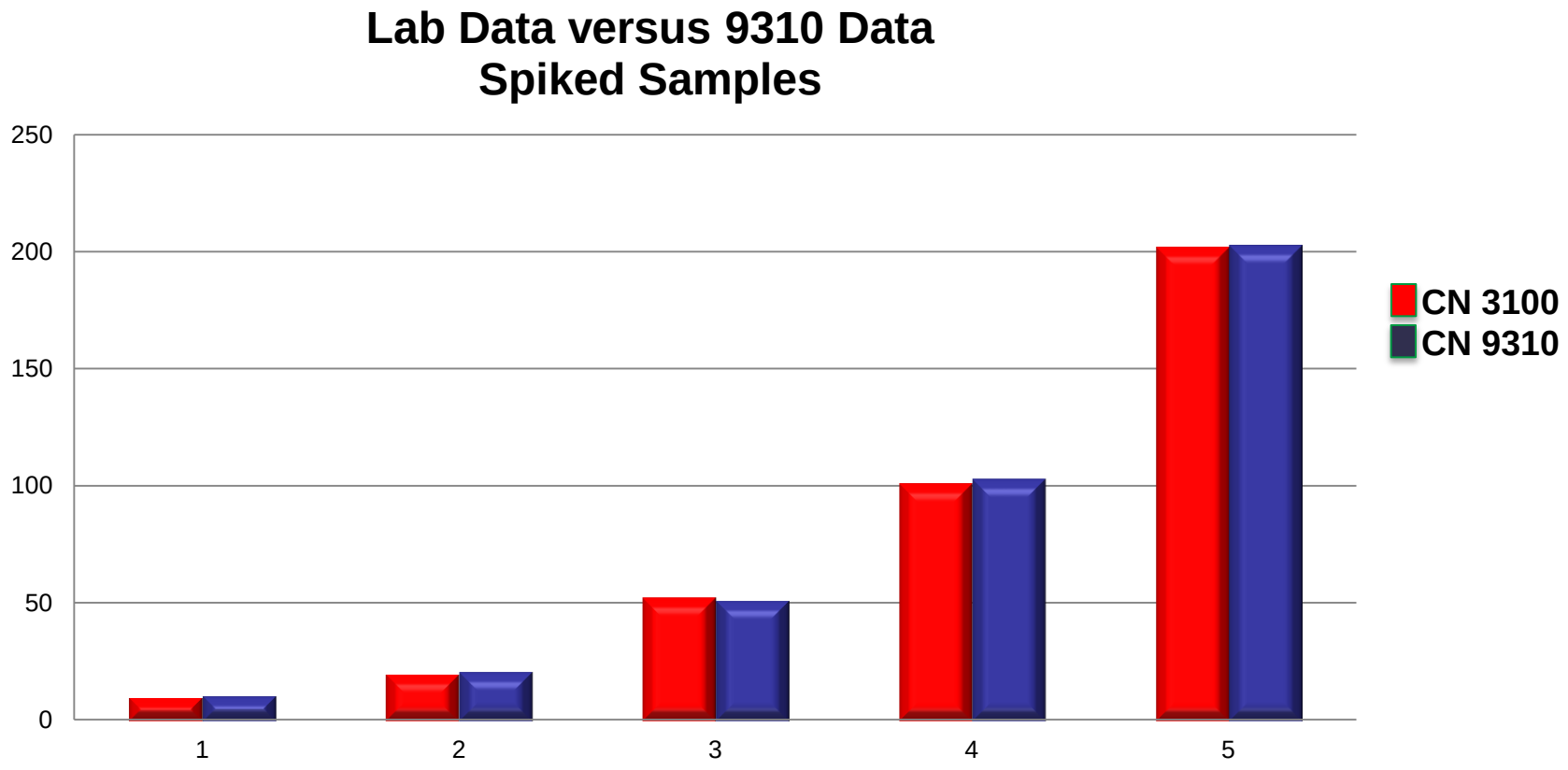
Repeatability (% RSD) of 5 Different CNSolution 9310 Analyzers

Standard	Instrument 1	Instrument 2	Instrument 3	Instrument 4	Instrument 5
2 ppm	3.5	1.1	2.6	3.8	1.7
5 ppm	1.3	0.73	0.8	5.4	0.9
10 ppm	0.7	3.19	0.9	5.4	1.9
20 ppm	1.1	1.38	3.4	3.4	1.8
50 ppm	1.7	1.02	1.4	2.7	1.3
100 ppm	0.6	0.43	0.3	3.6	1.7
200 ppm	0.4	3.61	0.4	2.8	1.4

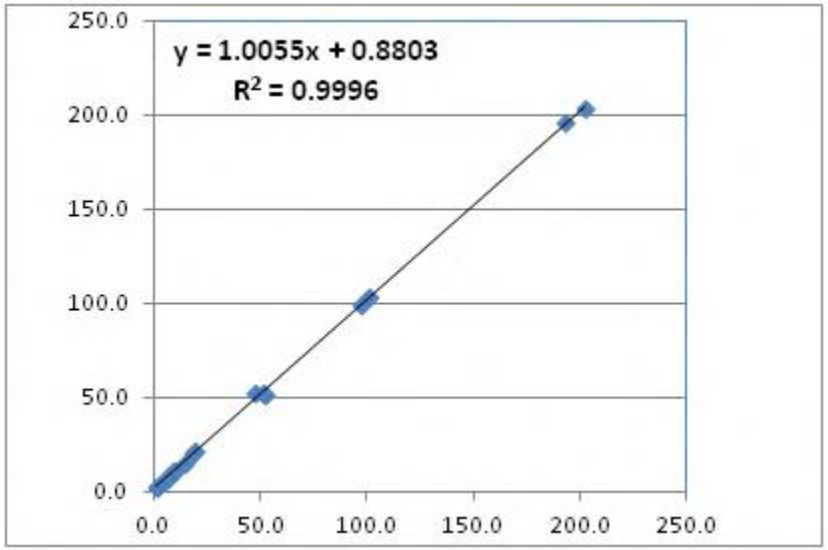
Matrix Used for On-line / Laboratory Equivalency Testing

Analyte	Result (mg/L)
pH	12.4 (S.U.)
NO_3-N	9.7
NH_3-N	13.0
OCN^-	196
SCN^-	206
TDS	8860

Data from On-line / Laboratory Equivalency Testing

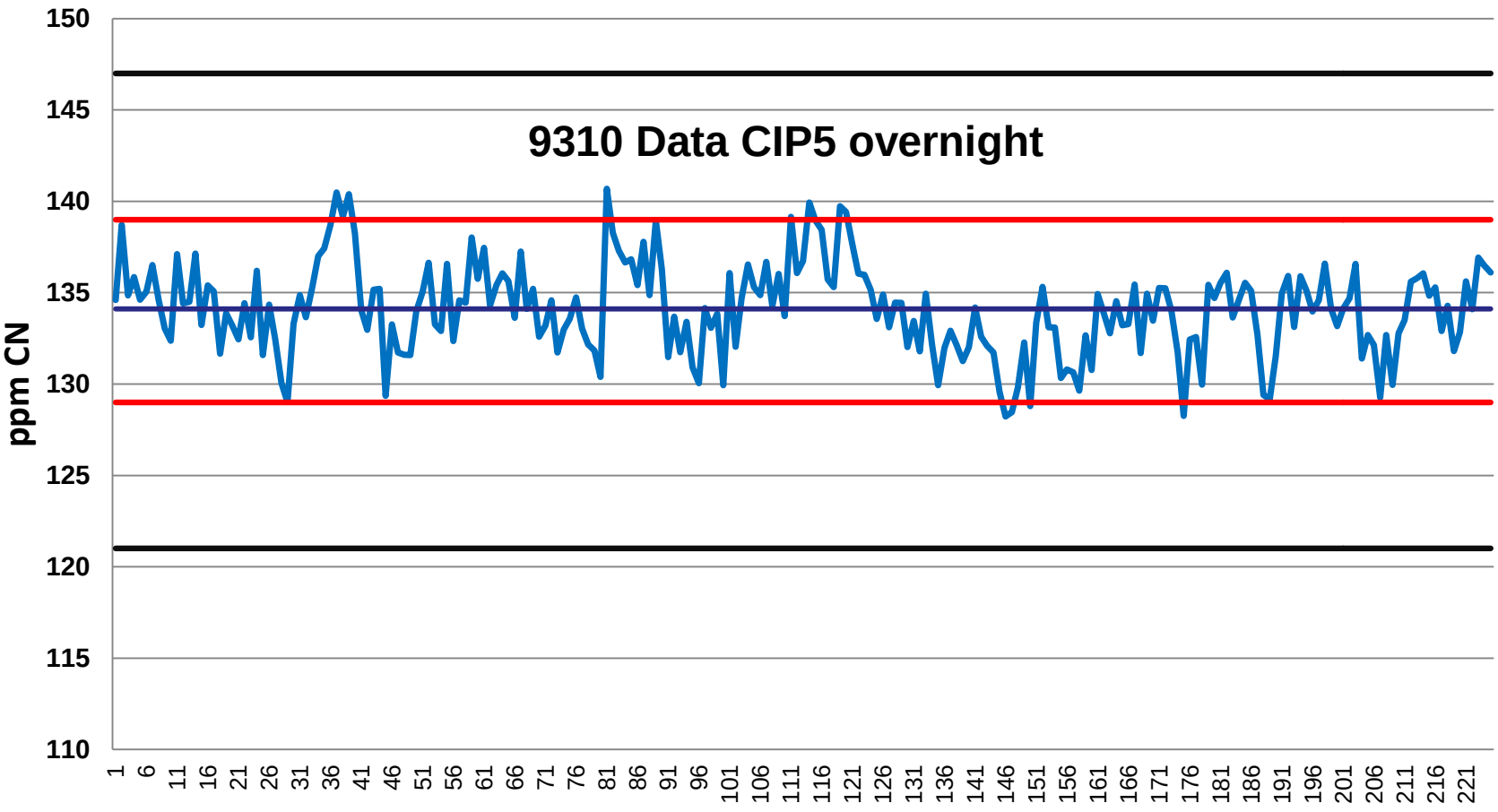


Data from On-line / Laboratory Equivalency Testing



Correlation of CNSolution 9310 On-line Analyzer and CNSolution 3100 Laboratory Analyzer

CNSolution 9310 Stability



Data from Carbon-In-Pulp (CIP) Leach Tank 5

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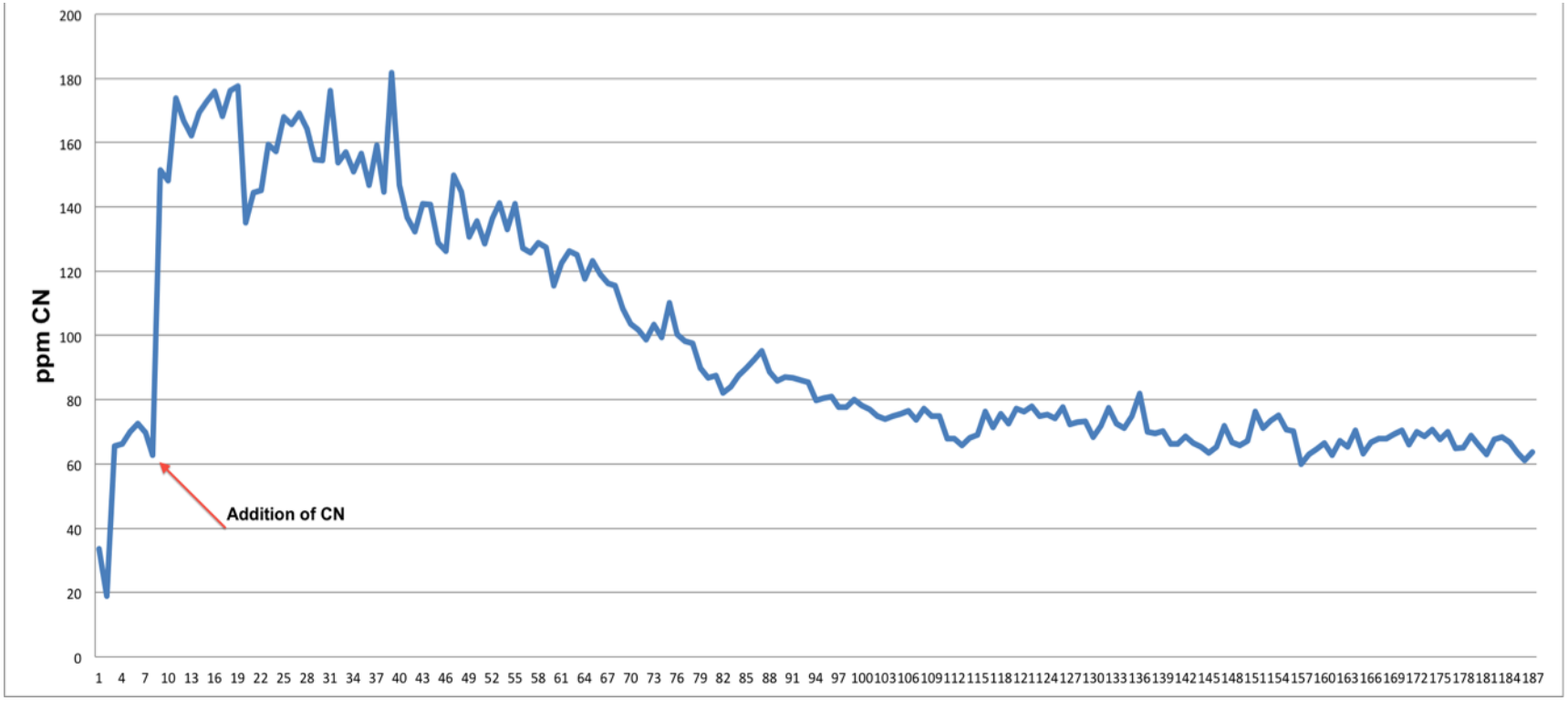
Loss of Cyanide During Leaching Measured by a 9310 On-line Cyanide Analyzer



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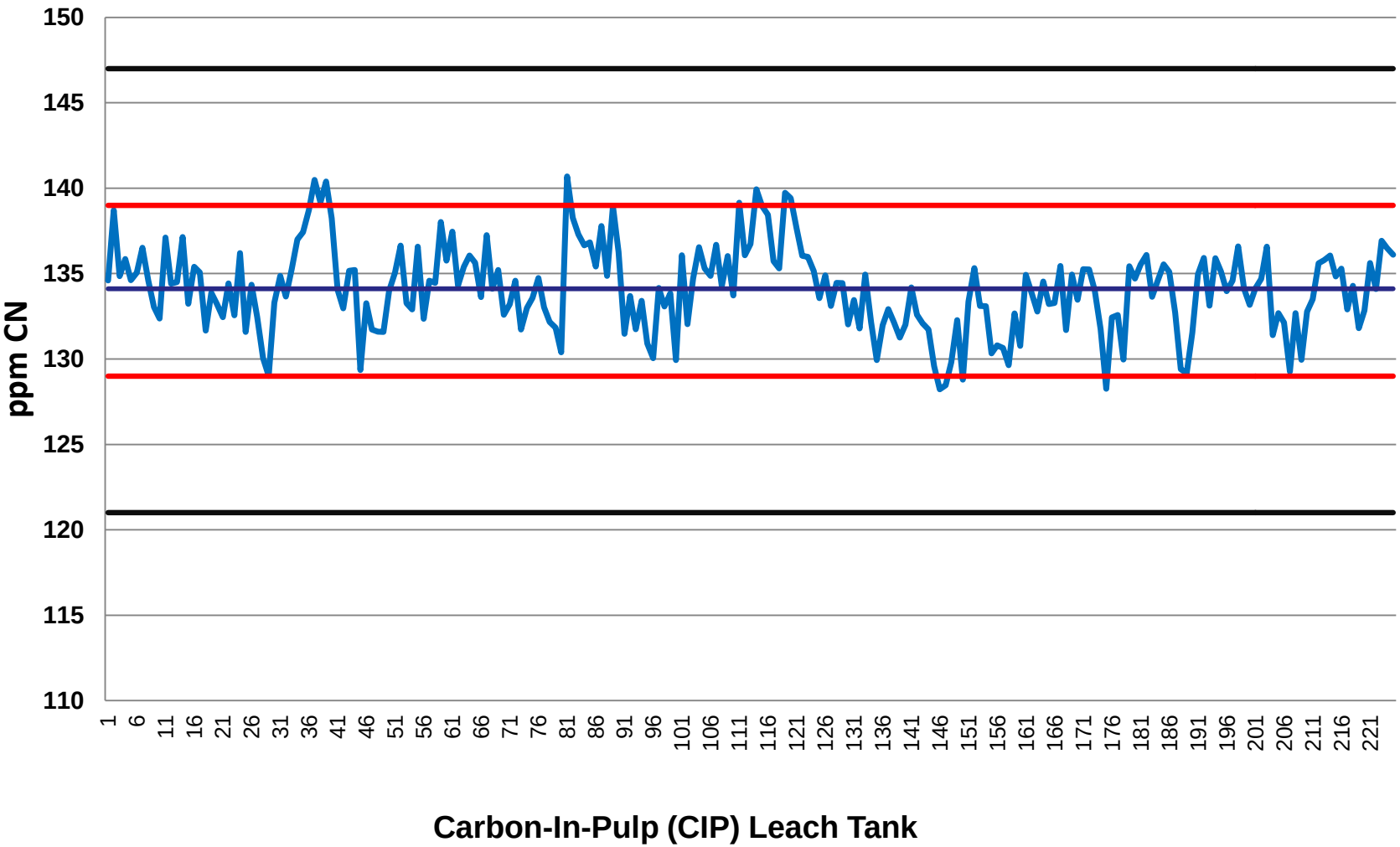
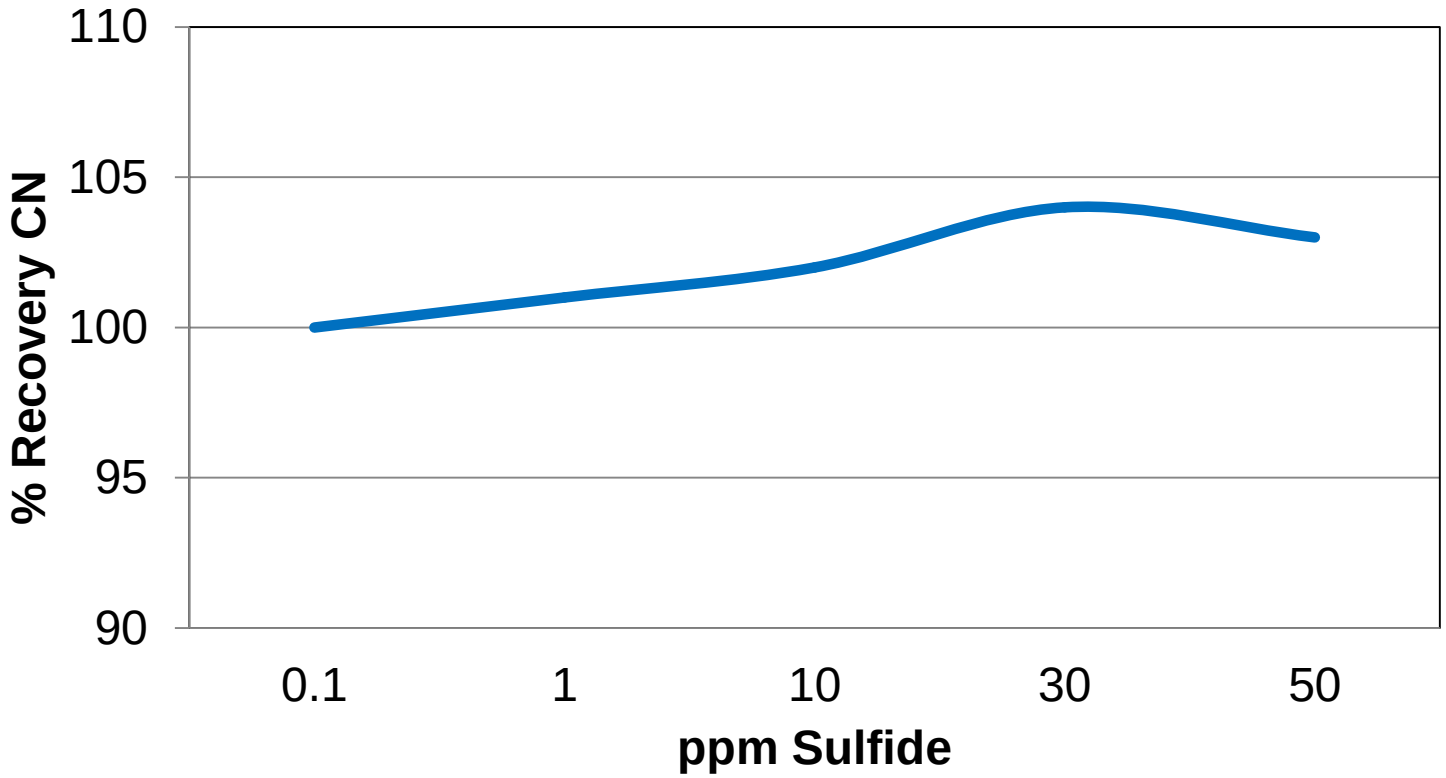
Example of Continuous CIP Leach Data



Precious Metal Detox Solutions Contain High Concentrations of Interfering Ions

Interference	Mg/L
Ni	0 - 1
NO_2-N	0 - 10
NO_3-N	0 - 10
S_2O_3	0 - 200
S_4O_6	0 - 100
SCN	0 - 500
SO_2	0 - 200

Up to 50 ppm Sulfide Does Not Interfere with Gas-Diffusion Amperometry Methods



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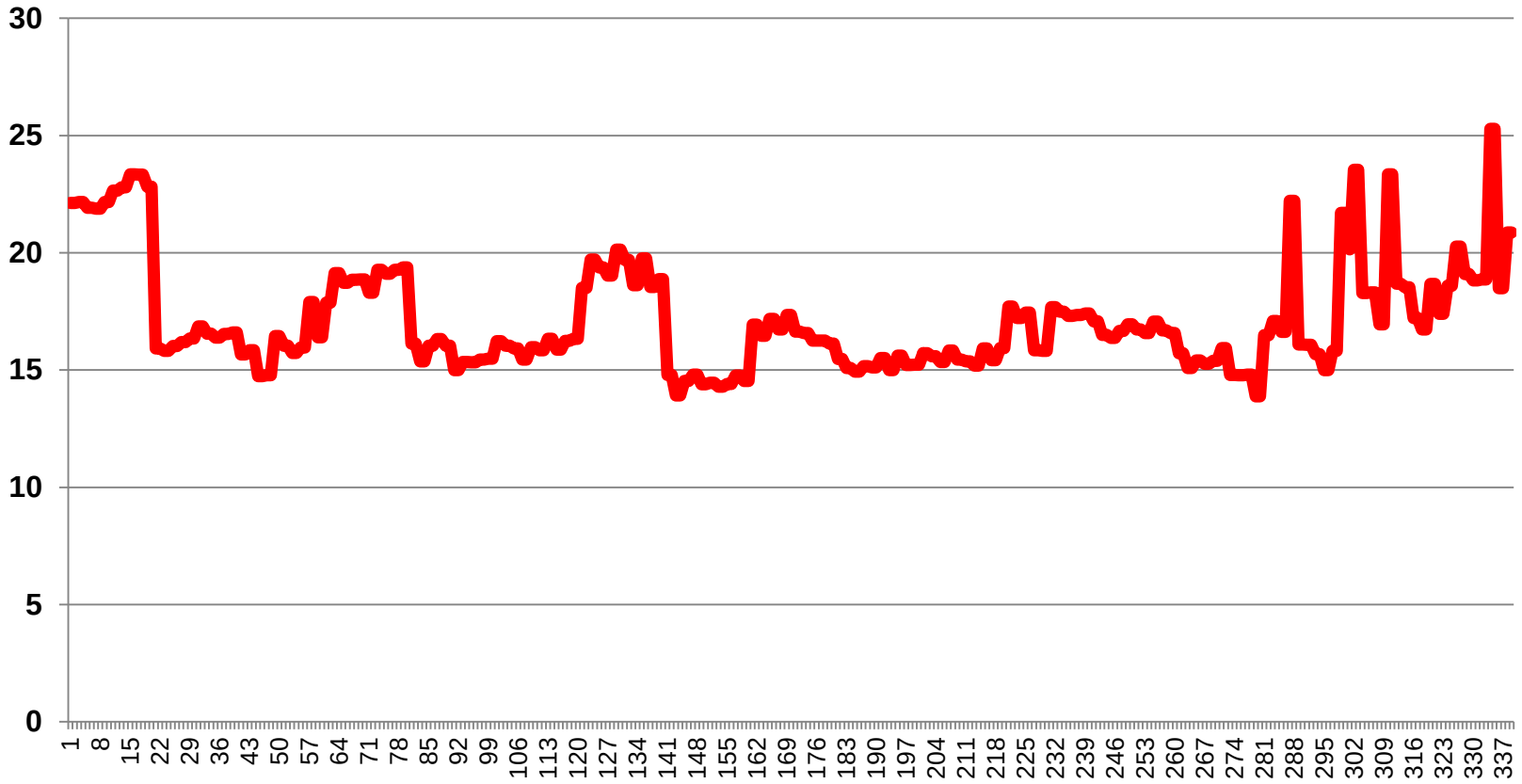
Example of Continuous Detox Effluent Data



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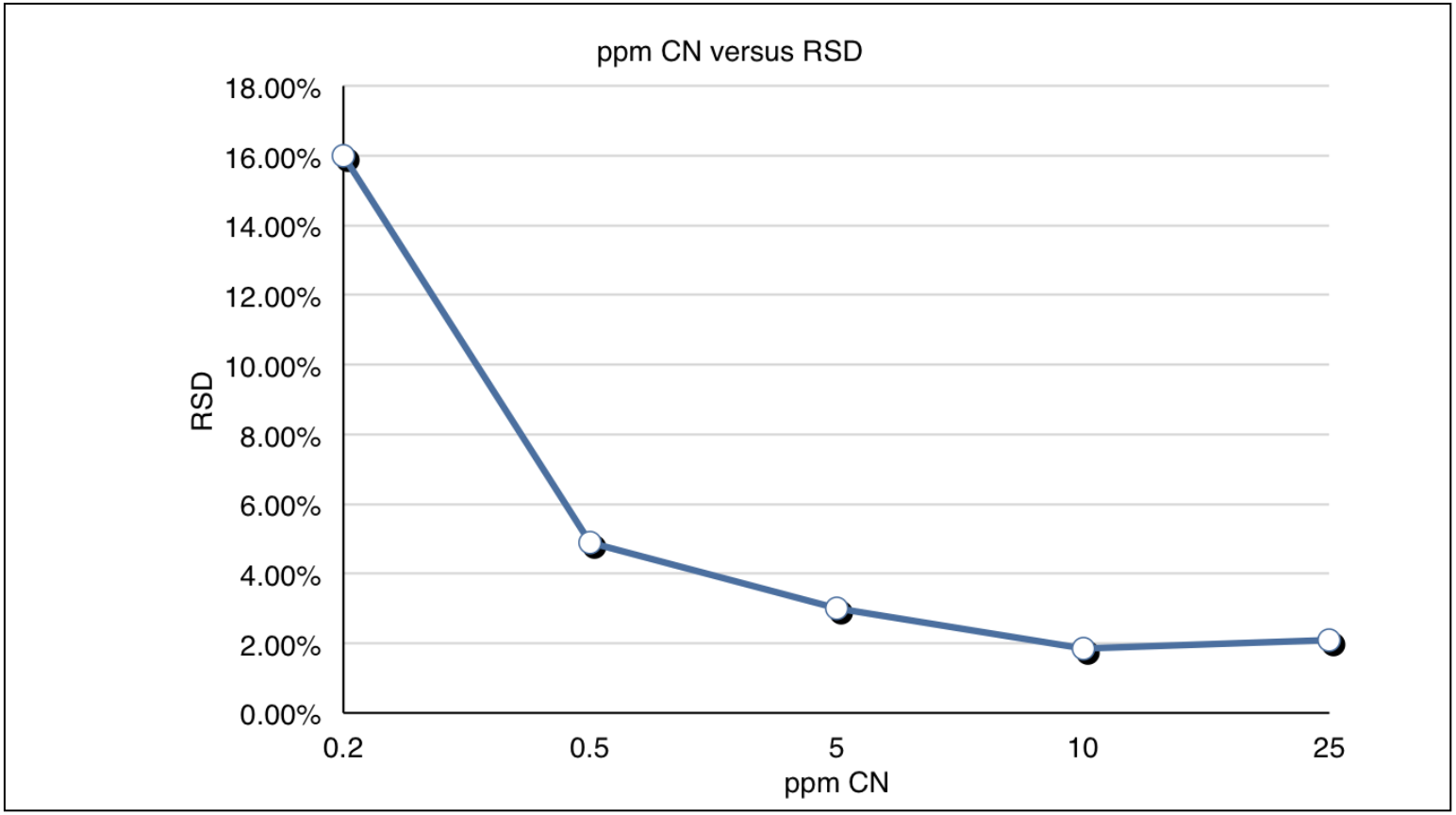
CNSolution 9310 On-line Cyanide Analyzer Low – Level Precision



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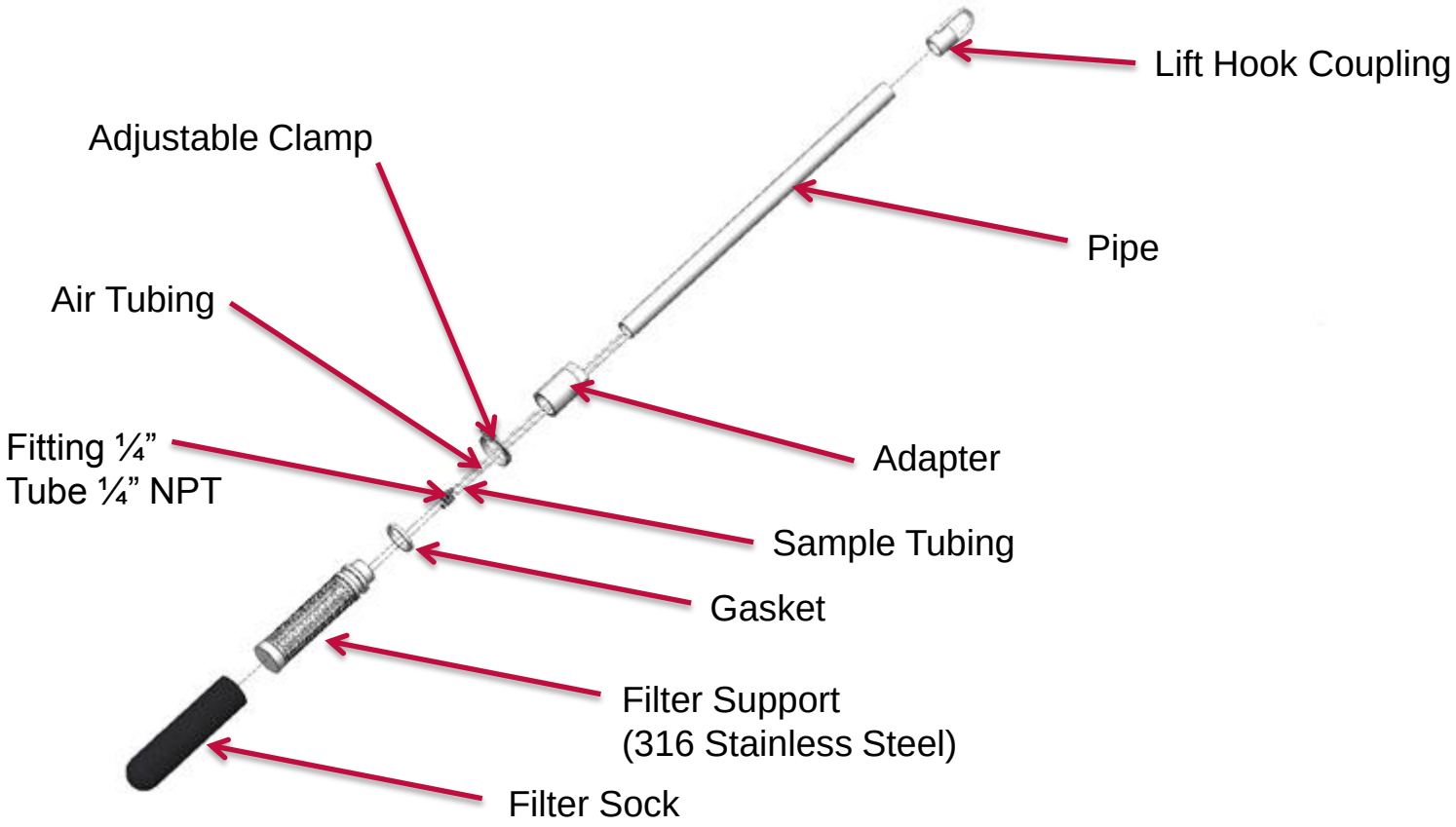
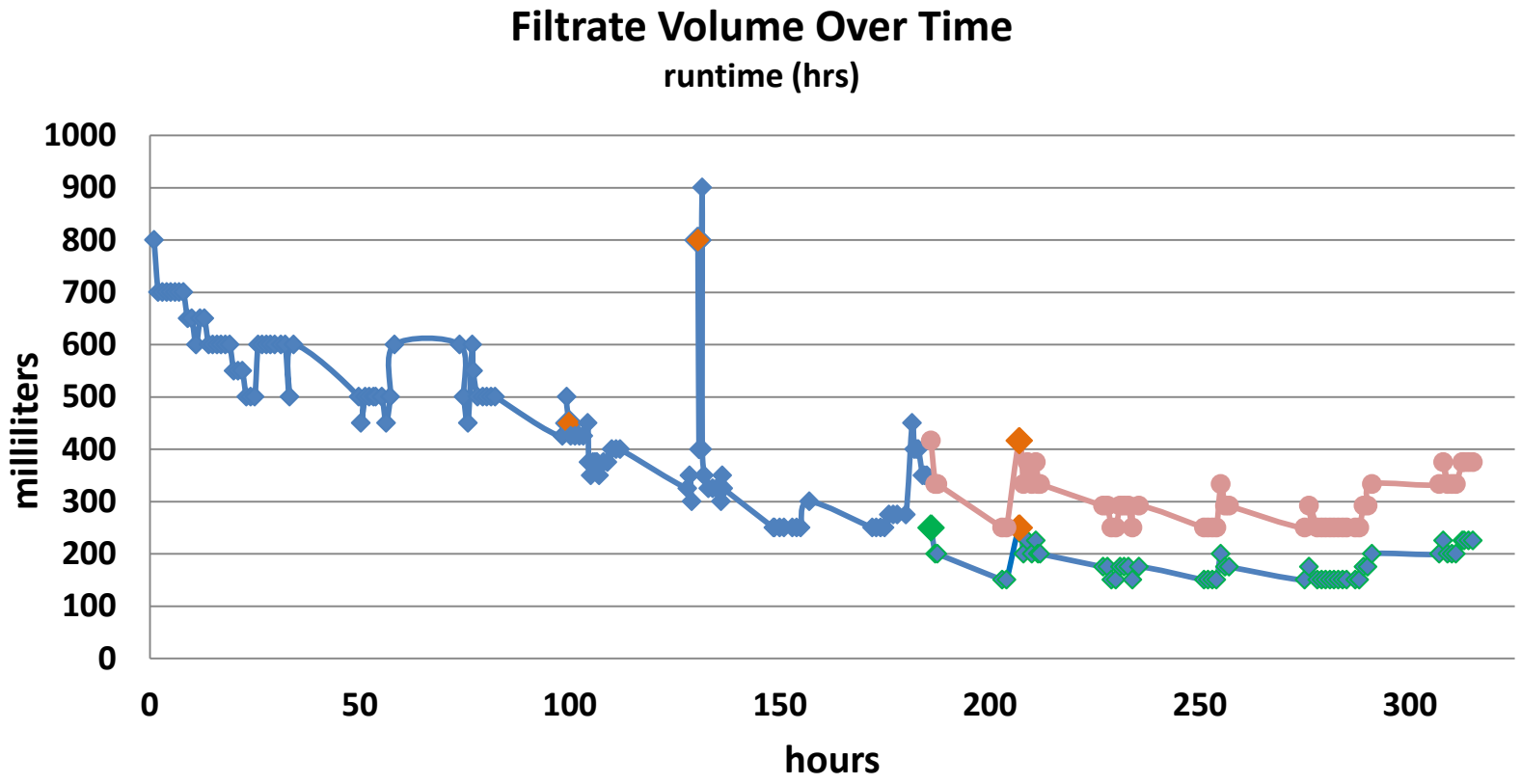
Slurry Filtration / Sampling System for CNSolution 9310 On-line Analyzer

- **60 % Solids**
- **< 10 microns**
- **2 minute cycle**

Exploded View of the CNSolution 9310 Filter Probe Assembly



Performance of CNSolution 9310 On-line Analyzer Sample Filtration System



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CNSolution 9310 On-line Cyanide Analyzer

- **9310 Analyzer**
- **Filtration Control Box**
- **Clean Filtrate Solution Pump**
- **50 Feet Tubing**
- **Stainless Steel Filter Probe**
- **Filters**
- **Environmental Cabinet / Enclosure**

Summary

U.S. EPA Method OIA-1677 and ASTM Method D 6888 accurately measure available cyanide in precious metal leaching and detox solutions.

Summary

An on-line cyanide analyzer for measuring available cyanide in leaching and detox solutions by U.S. EPA Method OIA-1677 and ASTM D 6888 is now available.

The CNSolution 9310 analyzer can be used as a benchtop analyzer for grab samples or deployed for on-line measurements and process control.

Questions?