An Alternative Method for Cyanide Analysis

Bruce Pelletier
President – Trace Analytical Laboratories

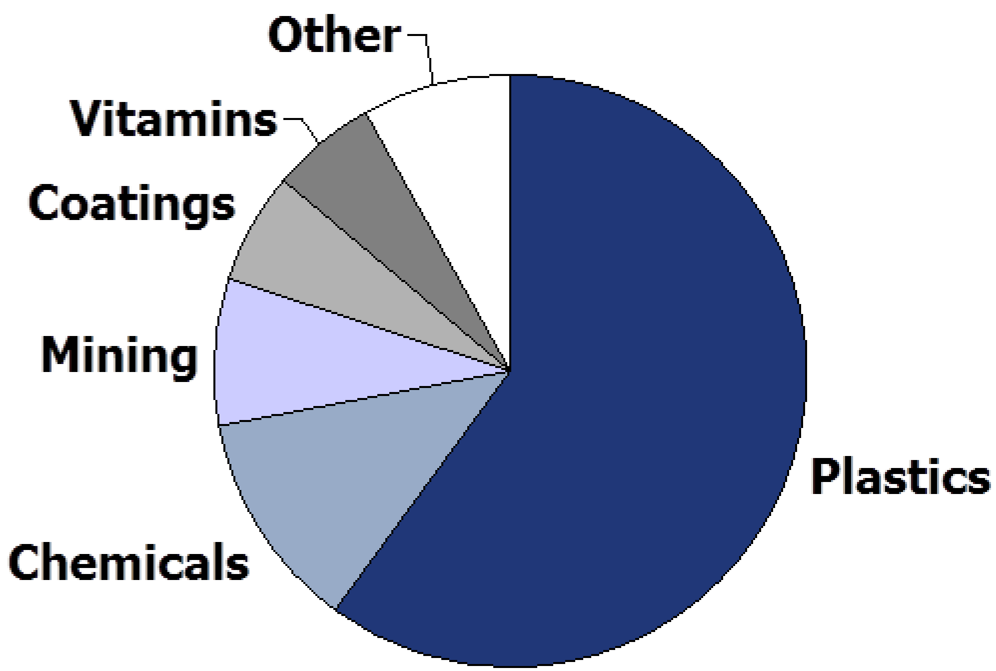
Total Cyanide is Regulated Because it can Generate Free Cyanide

Free Cyanide is a highly poisonous ion

Where does cyanide come from?

- Production of nylon
- Methyl methacrylate plastics
- Leach gold from ore
- Metal plating baths
- Petroleum refining
- Steel production
- Microelectronics
- Pharmaceuticals
- Specialty chemicals
- Pesticide production

Distribution of Industrial Uses of CN

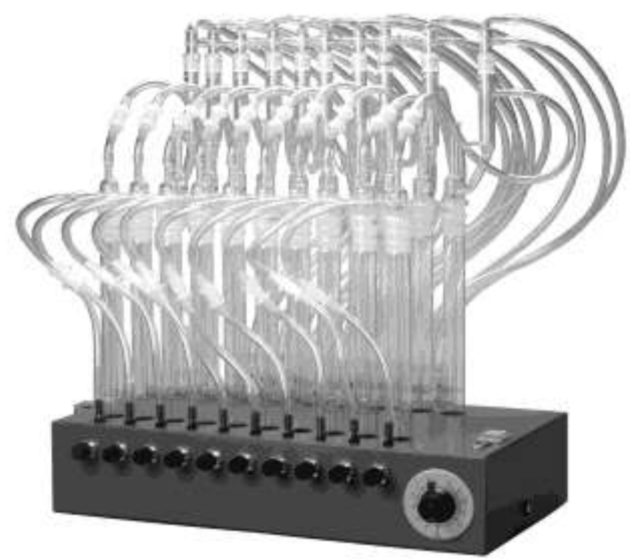


Cyanide methods require separation of CN from matrix

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

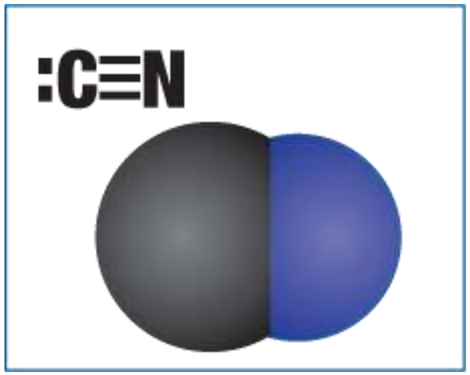
Distillation most common technique to remove interference

Macro Distillation



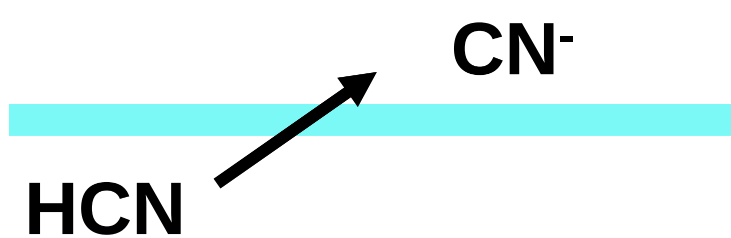
MIDI Distillations

This talk presents problems and solutions in cyanide analysis



1. What we measure

2. Problems



3. Solutions

Disadvantage with Distillation Methods

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

- Multiple Interferences

Interferences – Determinative Steps

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

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**

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^-**

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%**

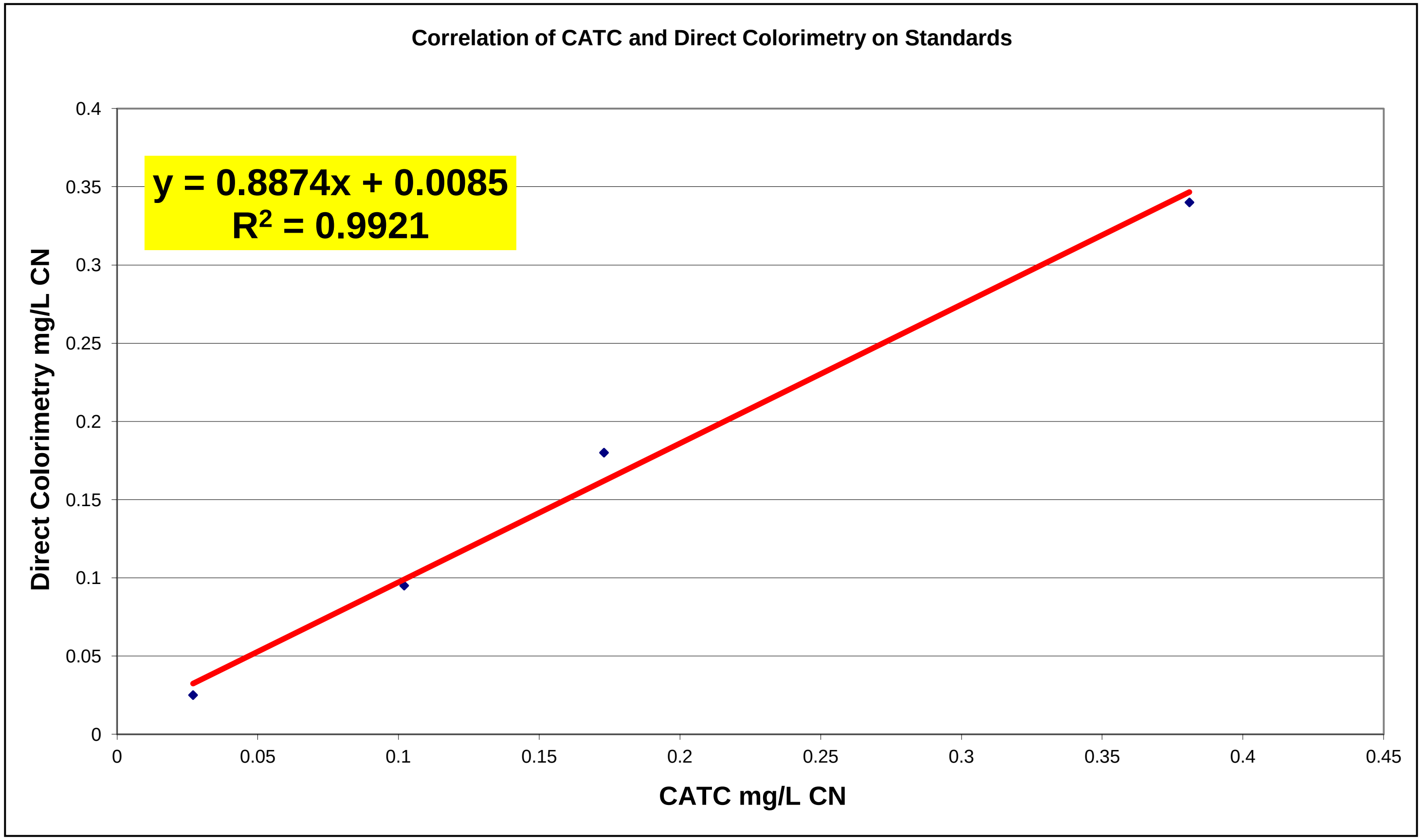
- **This reaction occurs in absorber solution, or in preserved sample**

There is no way to "know" if sulfur compounds are present

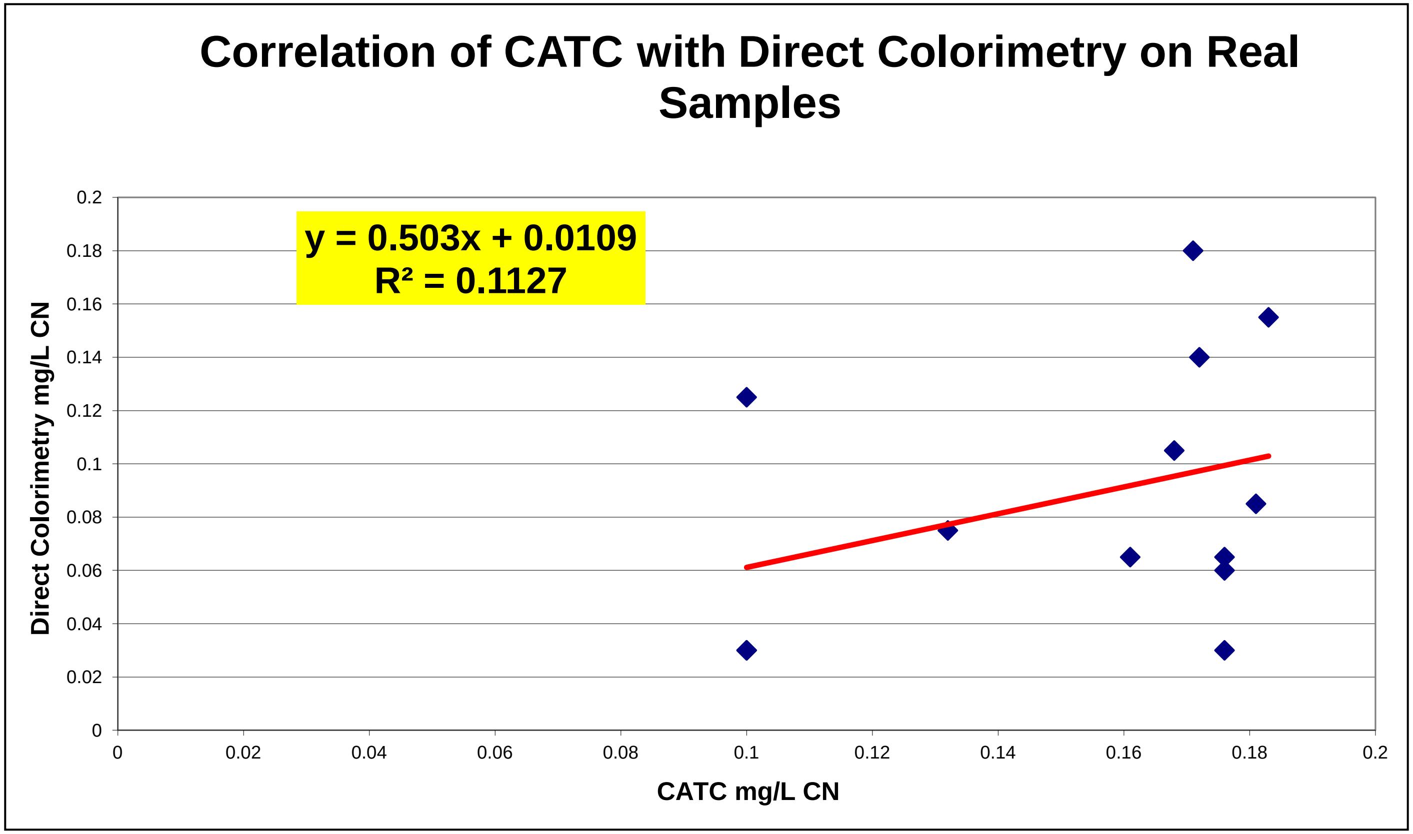
- No "spot" tests that adequately detect the sulfur compounds
- Sodium sulfite and sodium thiosulfate are both added to samples for dechlorination.

Why again do we need more cyanide methods?

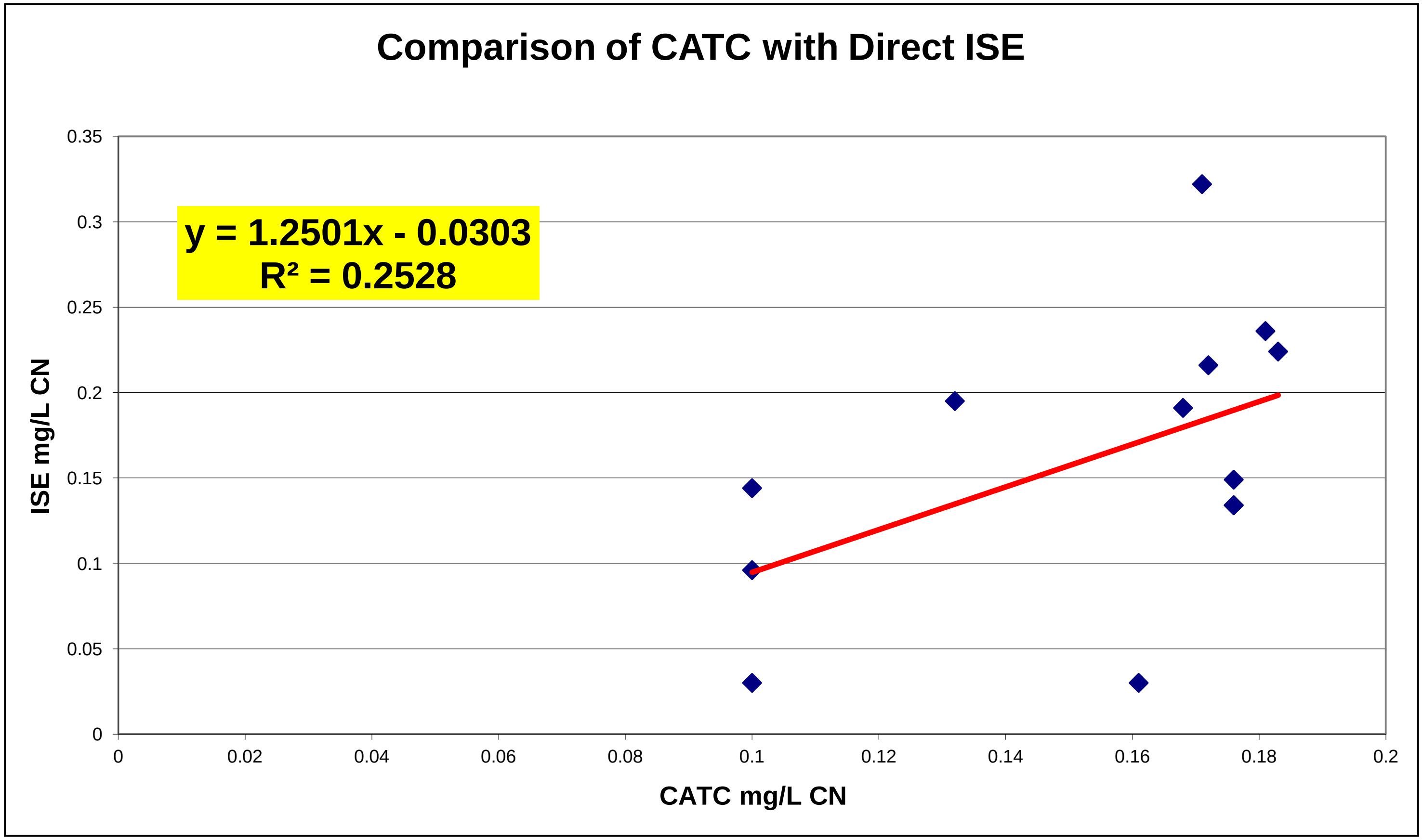
If all we had was CN^- in dilute NaOH it would be easy



Direct colorimetry does not correlate with distillation results



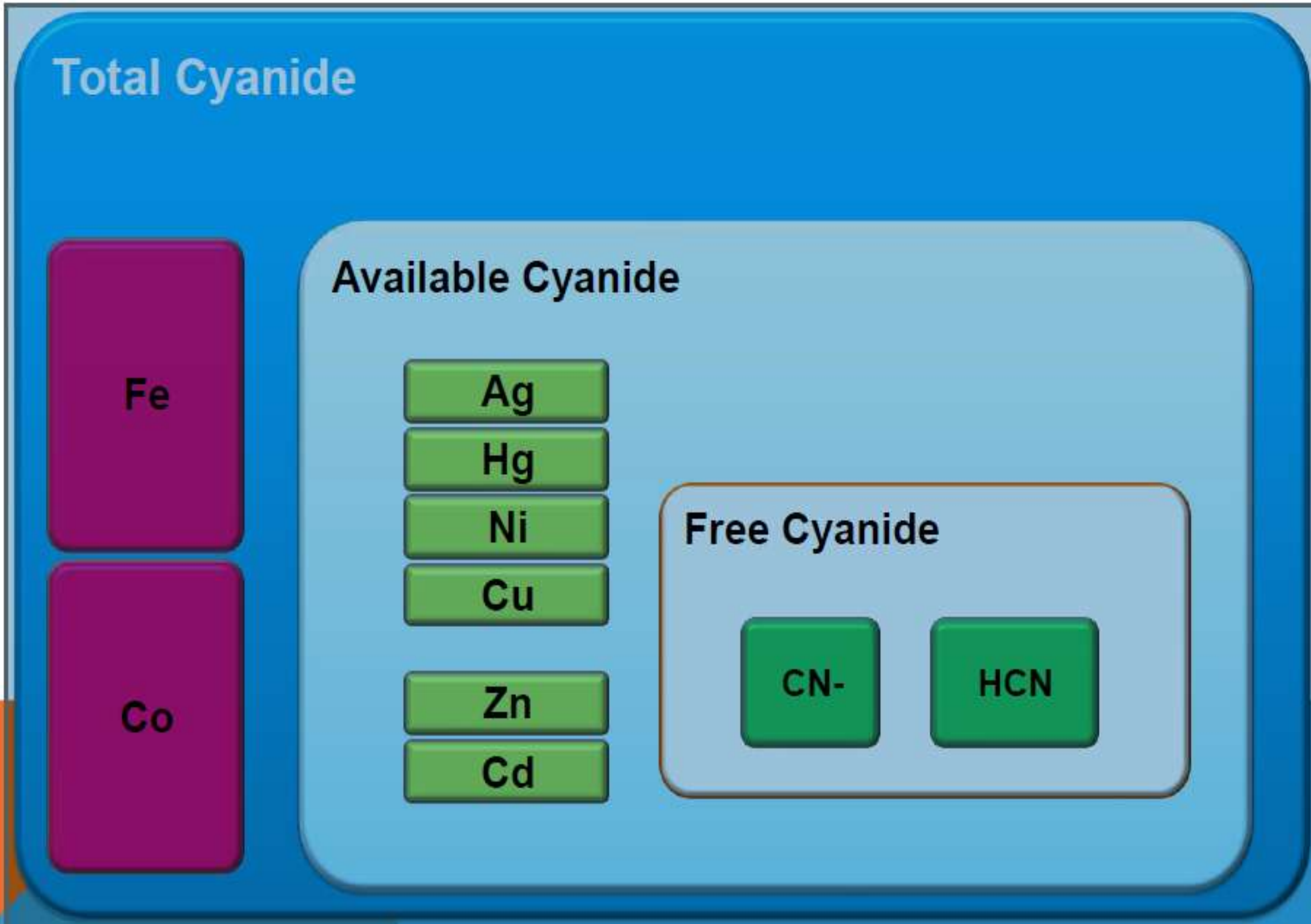
Direct ISE does not correlate with distilled real sample results



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^-

Cyanide methods should measure metal-cyanide complexes that share chemical characteristics



Footnote 6 (MUR 2007) allows other methods to be used

- On April 17th, 2012, the U.S. EPA Administrator signed a Methods Update Rule (MUR) approving new analytical methods for testing of pollutants in wastewater under the Clean Water Act.
- Six ASTM methods (including ASTM D 7511-09e2) covering sampling, preservation, and analysis of free, available and total cyanide species
- Facilities with National Pollutant Discharge Elimination System (NPDES) permits can now use ASTM D 7511-09e2 to test wastewater samples for regulatory compliance reporting.

Iron cyanide is not toxic.

- **Sunlight causes iron cyanide to release HCN**
- **Sunlight = UV irradiation**

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

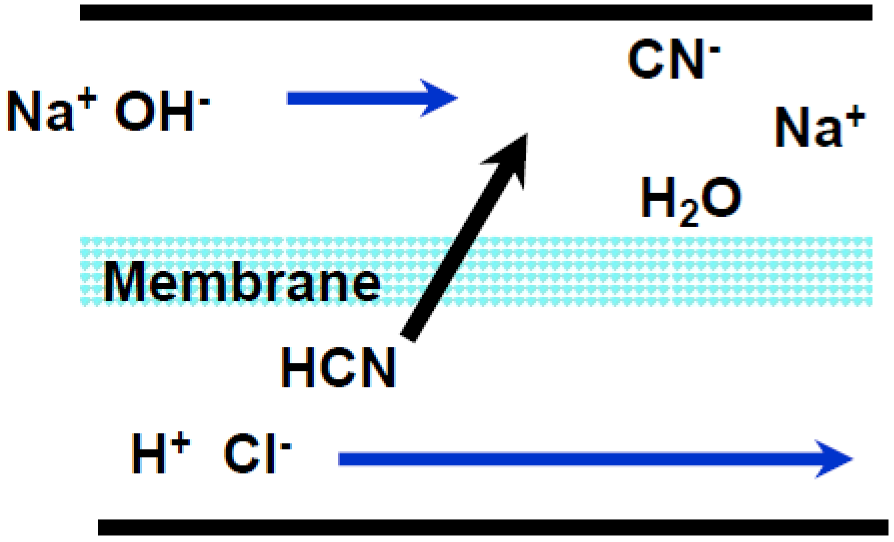
Automated total cyanide methods use UV to liberate HCN from Fe

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

The old (Manual Distillation)

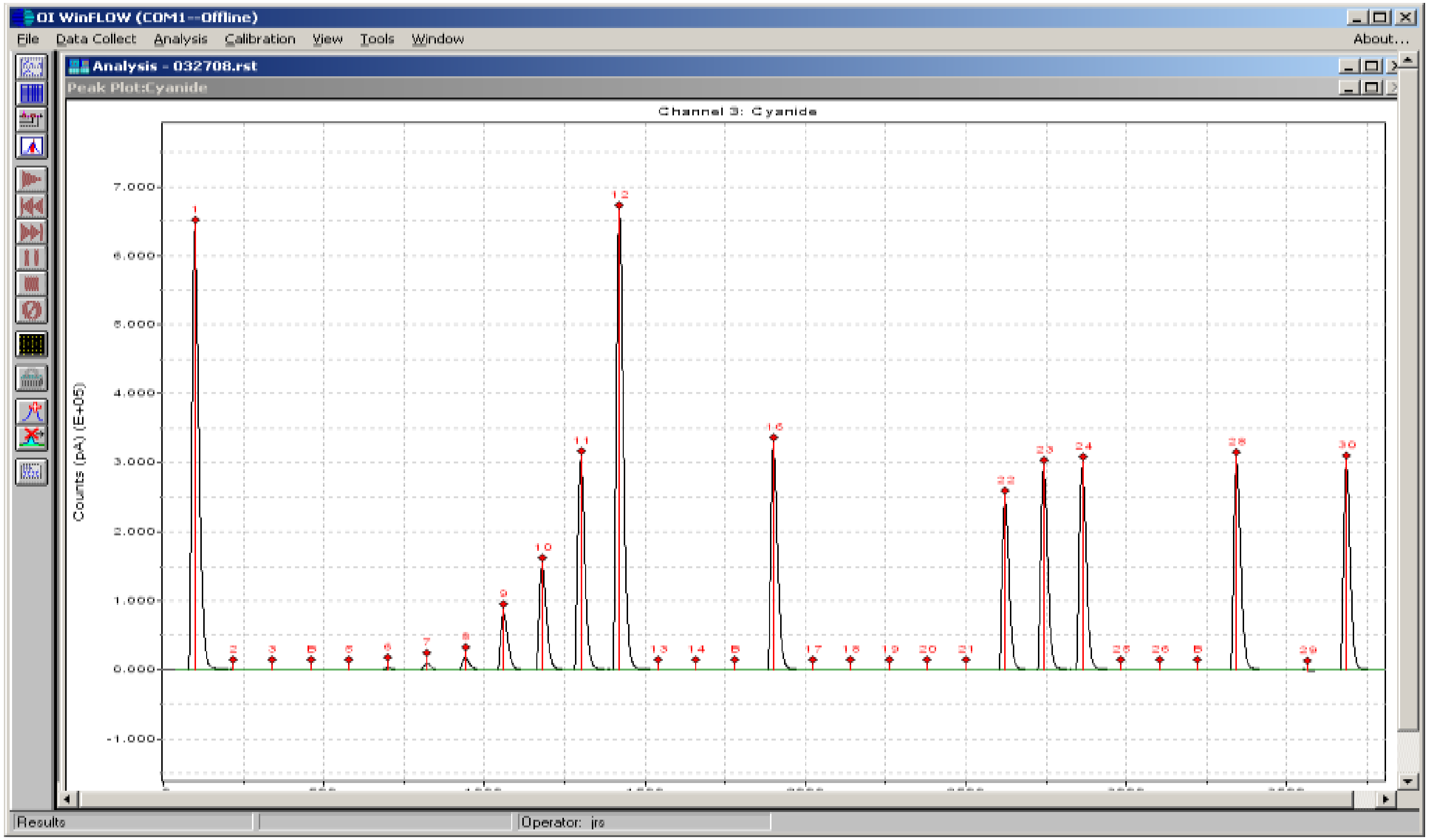
Purging and boiling in acid

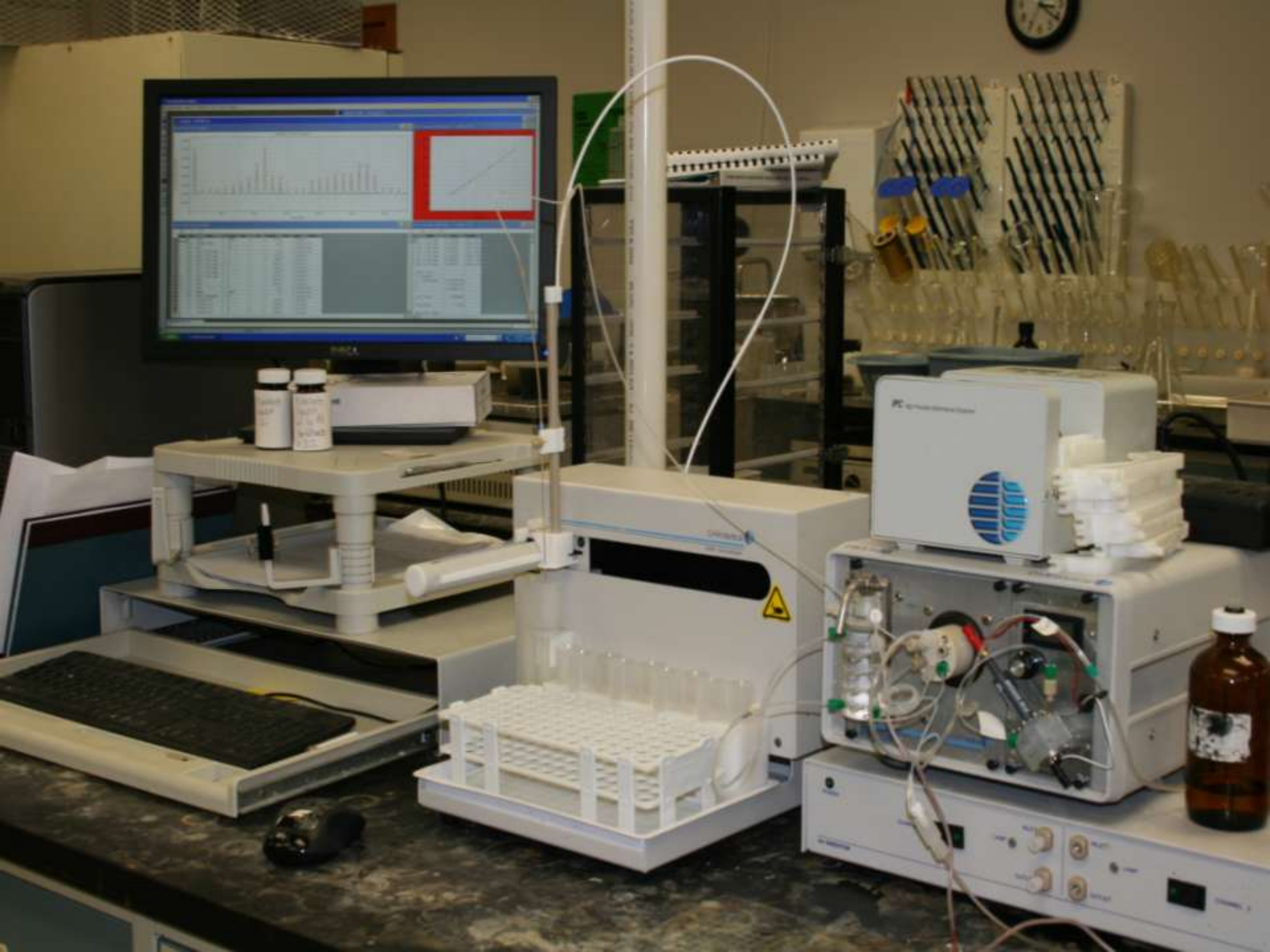
Or Automated gas diffusion

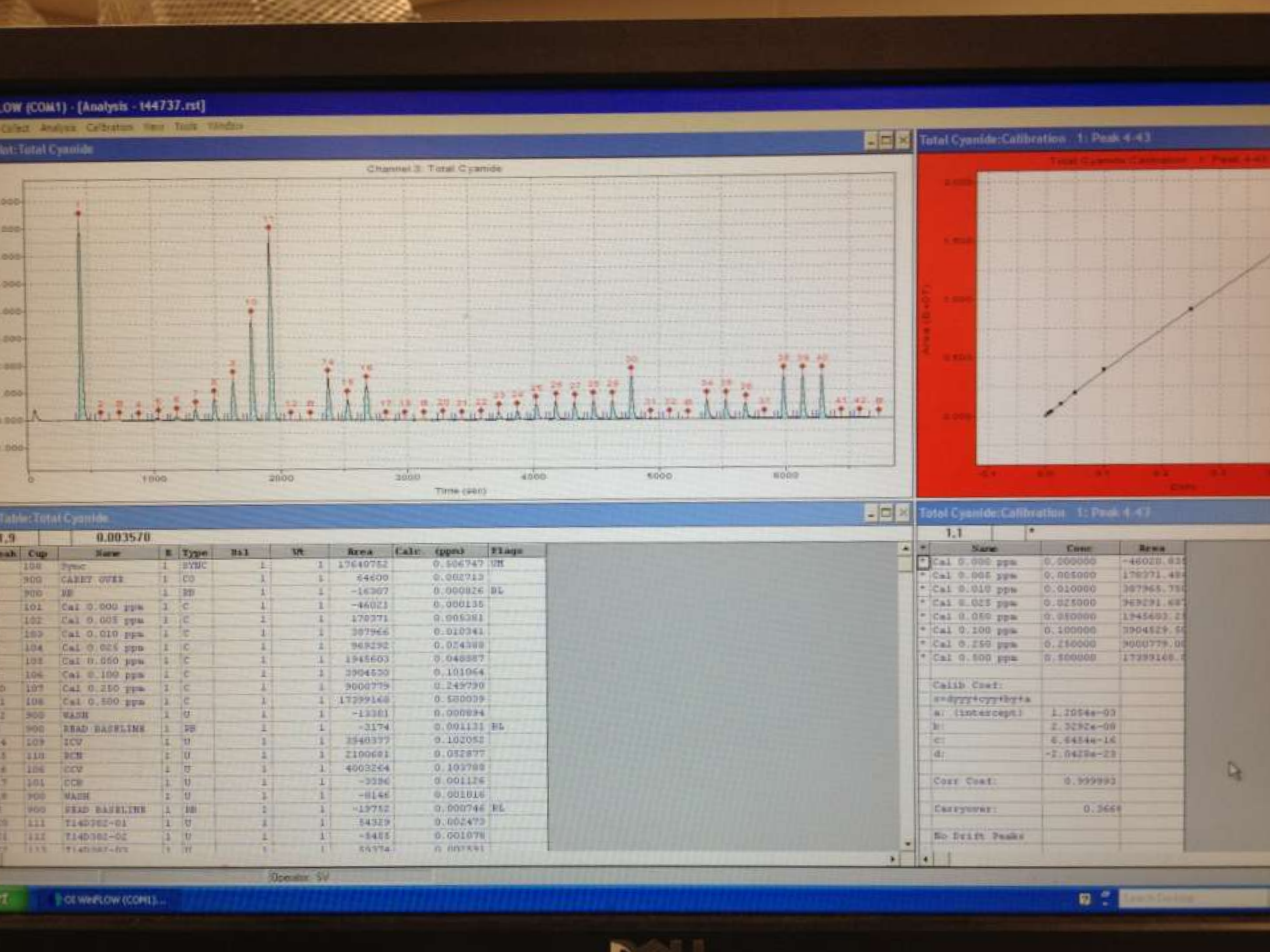


Electrochemistry techniques integrate matrix removal

- **Very sensitive with large dynamic range.**







LOW (COM1) - [Analysis - t44737.rst]
Total Cyanide
Channel 3: Total Cyanide
Time (sec)
Total Cyanide:Calibration 1: Peak 4-43
Table:Total Cyanide
0.003570
Cup Name R Type Bsl Wt Area Calc (ppm) Flags
108 Sync 1 SYNC 1 1 17640752 0.506747 UM
900 CARRY OVER 1 CO 1 1 64600 0.002713
900 RB 1 RB 1 1 -16307 0.000826 BL
101 Cal 0.000 ppm 1 C 1 1 -46021 0.000135
102 Cal 0.005 ppm 1 C 1 1 170371 0.005381
103 Cal 0.010 ppm 1 C 1 1 387966 0.010341
104 Cal 0.025 ppm 1 C 1 1 969292 0.024388
105 Cal 0.050 ppm 1 C 1 1 1945603 0.048887
106 Cal 0.100 ppm 1 C 1 1 3904530 0.101064
107 Cal 0.250 ppm 1 C 1 1 9000779 0.249790
108 Cal 0.500 ppm 1 C 1 1 17299168 0.500039
900 WASH 1 U 1 1 -13381 0.000894
900 READ BASELINE 1 RB 1 1 -3174 0.001131 BL
109 ICV 1 U 1 1 3540377 0.102052
110 RCB 1 U 1 1 2100681 0.052877
106 CCV 1 U 1 1 4003264 0.103788
101 CCB 1 U 1 1 -3386 0.001126
900 WASH 1 U 1 1 -8146 0.001016
900 READ BASELINE 1 RB 1 1 -13752 0.000746 BL
111 T140382-01 1 U 1 1 54329 0.002473
112 T140382-02 1 U 1 1 -5455 0.001078
Total Cyanide:Calibration 1: Peak 4-47
1.1
Name Conc Area
Cal 0.000 ppm 0.000000 -46020.83
Cal 0.005 ppm 0.005000 170371.48
Cal 0.010 ppm 0.010000 387965.75
Cal 0.025 ppm 0.025000 969291.68
Cal 0.050 ppm 0.050000 1945603.2
Cal 0.100 ppm 0.100000 3904529.5
Cal 0.250 ppm 0.250000 9000779.0
Cal 0.500 ppm 0.500000 17299168.
Calib Coef:
x=dyyy+cyy+by+a
a: (intercept) 1.2054e-03
b: 2.3292e-08
c: 6.6454e-16
d: -2.0429e-23
Corr Coef: 0.999993
Carryover: 0.366
No Drift Peaks
Operator: SV
OI WinFLOW (COM1)...