Reducing Interferences in Cyanide Analysis

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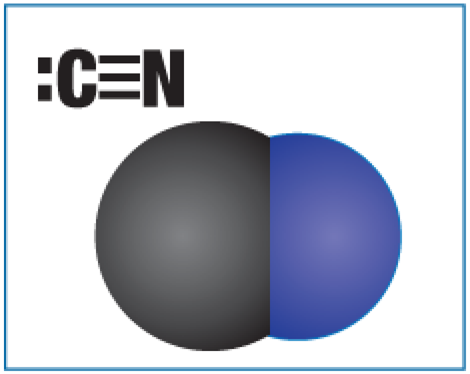
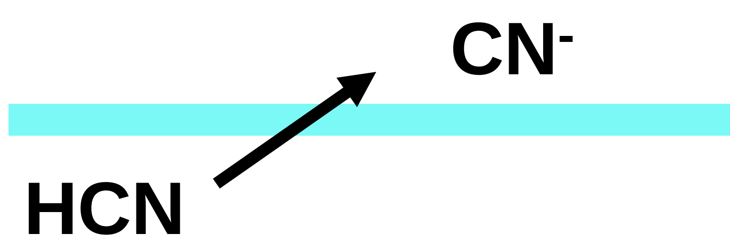
A World of Solutions

This talk presents problems and solutions in cyanide analysis



1. What we measure

2. Problems



3. Solutions

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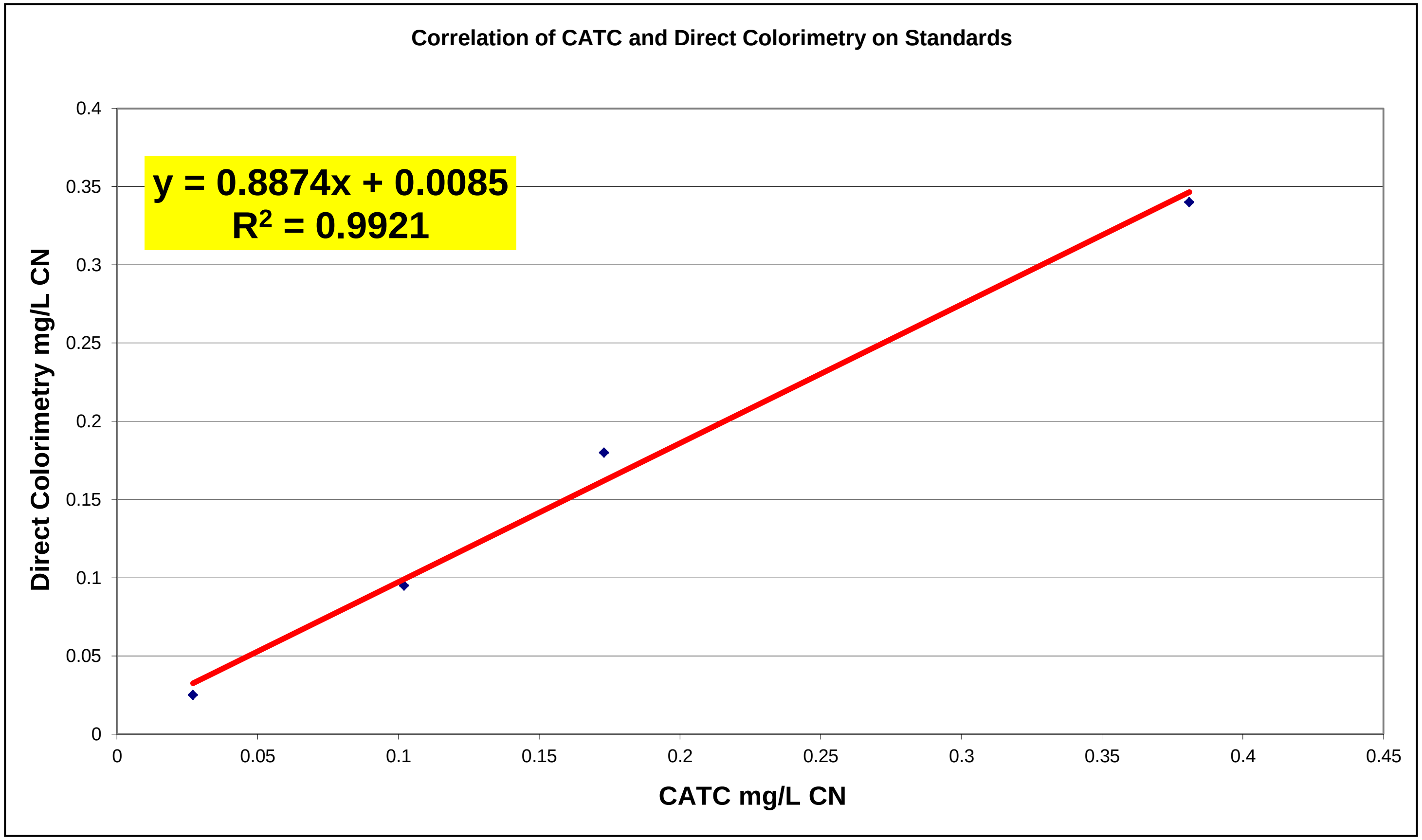
Cyanide methods measure the various cyanide “species”

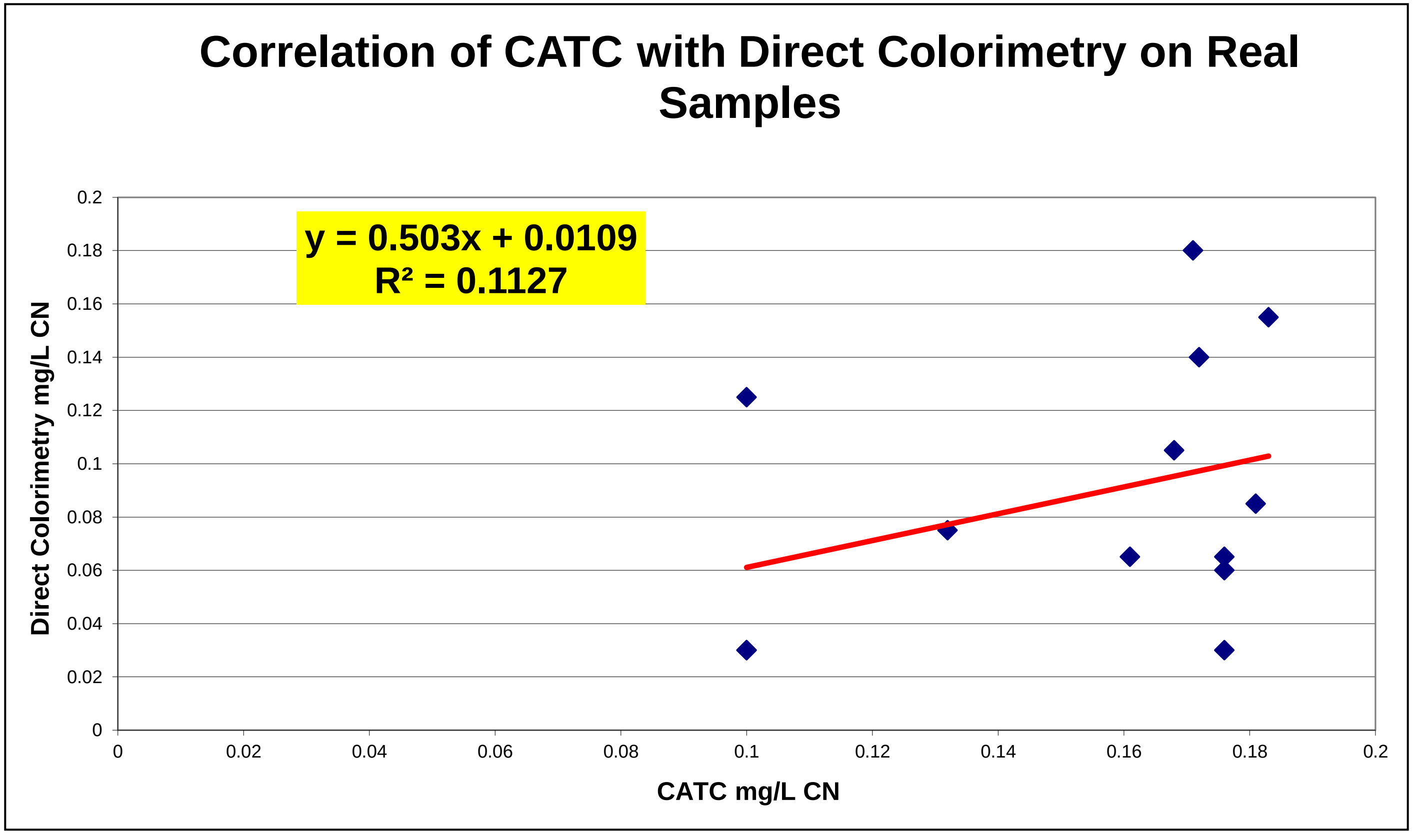
Total CN

- **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^-

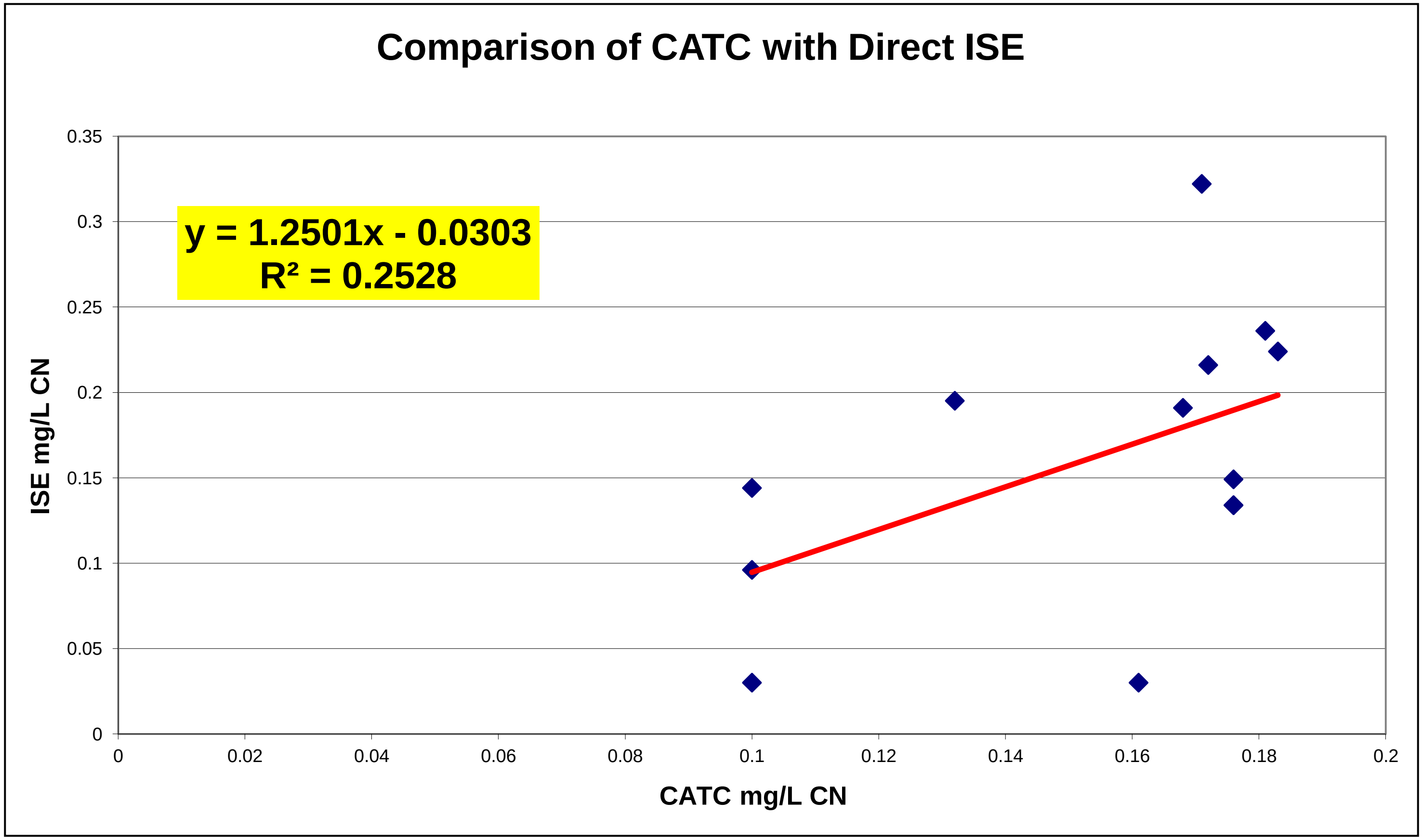
If all we had was CN^- in dilute NaOH it would be easy



Direct colorimetry does not correlate with distillation results



Direct ISE does not correlate with distilled real sample results

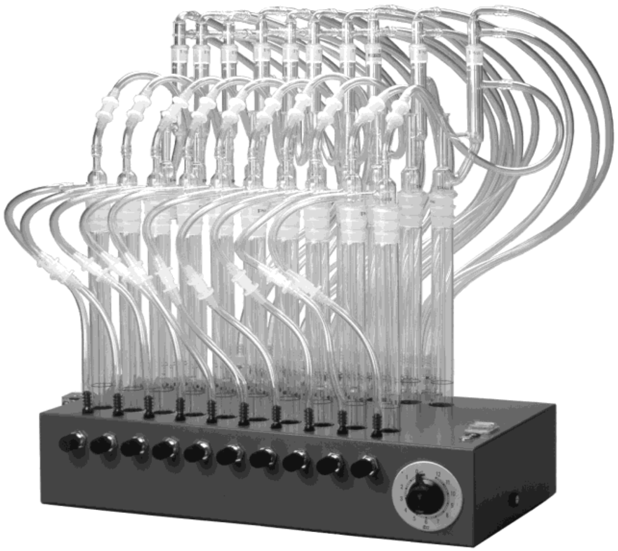


Cyanide methods require separation of CN from matrix

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

Distillation most common technique to remove interference

Macro Distillation



MIDI Distillations

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Distillation actually creates CN interferences

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

Interferences with distillation are in almost every sample

- Thiocyanate
- Sulfur
- Thiosulfate/Sulfite
- Oxidizers

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**

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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^-

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.

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

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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.

Oxidizers destroy cyanide before or during distillation

- Hypochlorite
- Peroxide
- Caro’s Acid
- Chloramines

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

- More accurate?
  - Spikes?
- "challenge matrix" distilled

Matrix spikes cannot be used to demonstrate accuracy

Method	Amount Detected (ppb)	Recovery
335.4	32	98 %
335.3	16	98 %

Both methods detected CN^- in a synthetic sample with no CN^-.

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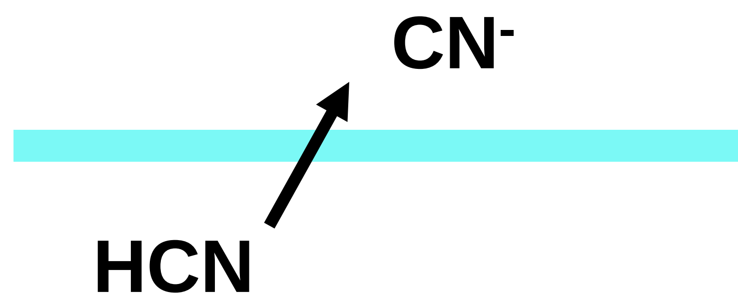
Verify Accuracy Using Interference Free Methods

- **Use methods demonstrated by literature and multiple users to be interference free**
  - **OIA 1677 or ASTM D6888-04**
  - **ASTM D 7284-08**
  - **OIA 1678 (ASTM D7511-09)**

The old versus the new

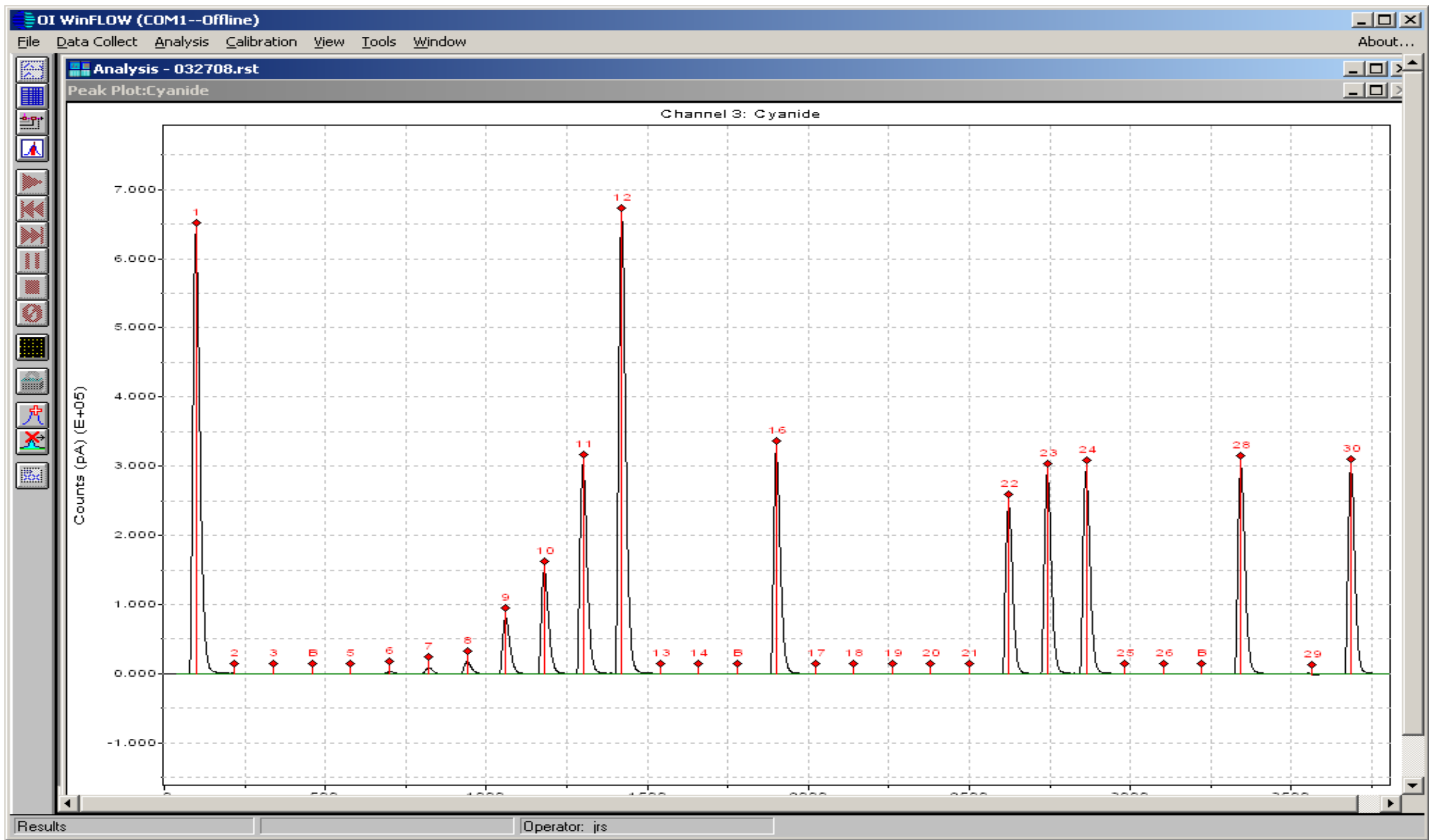
Purging and boiling in acid



Diffusion at room temperature

Electrochemistry techniques integrate matrix removal

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



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

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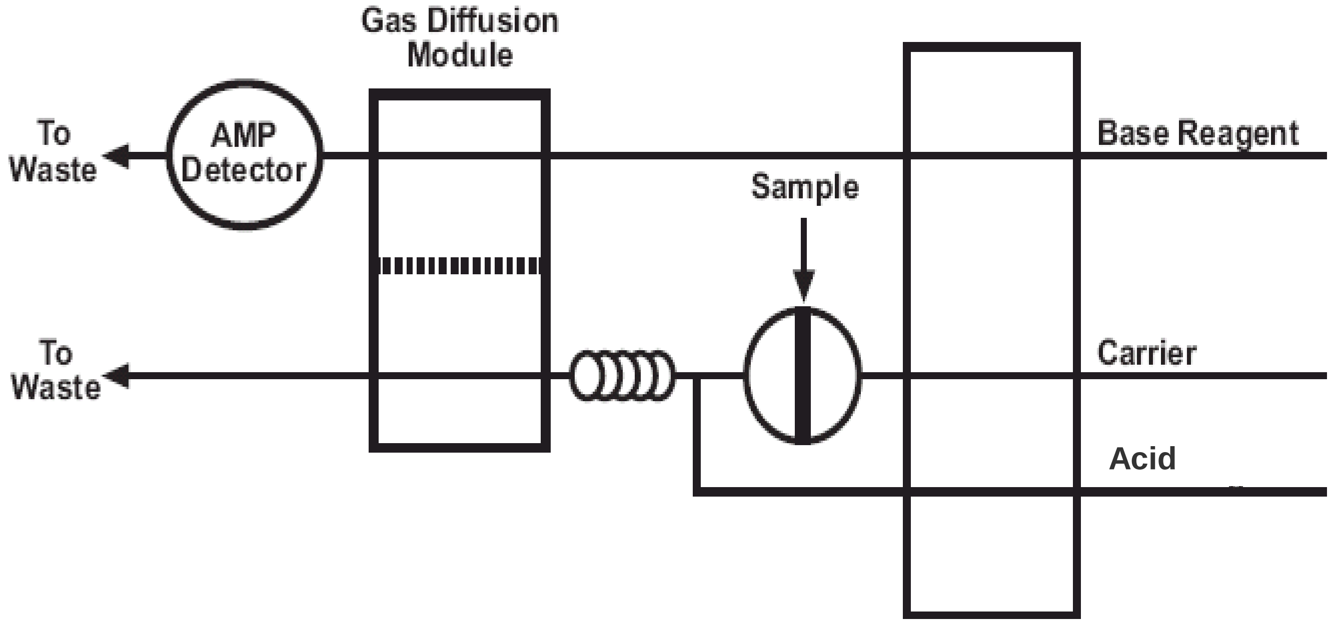
This flow diagram illustrates the simplicity of GD-amperometry



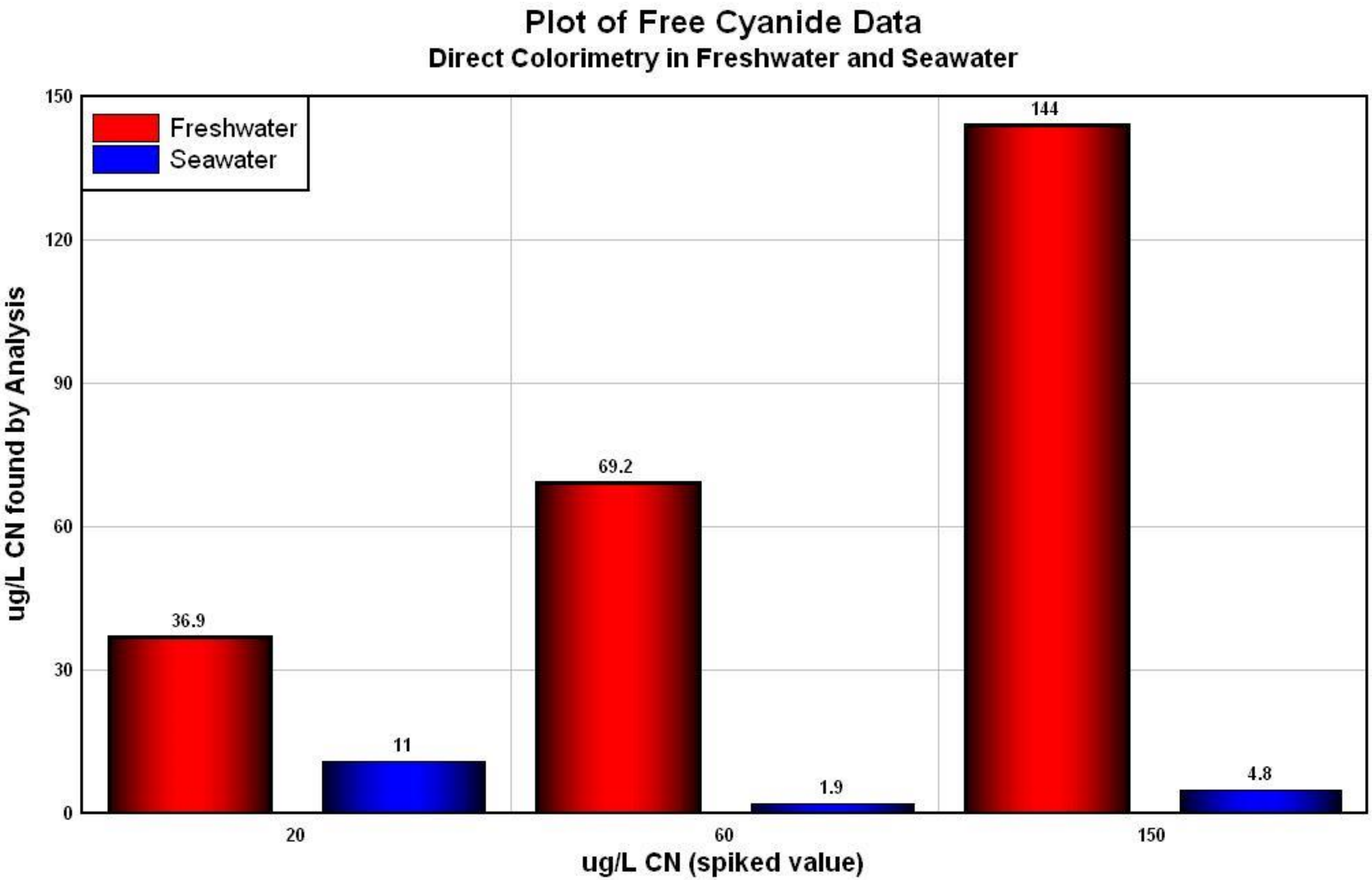
A series of GD-amperometry CN methods to meet needs

- Free cyanide
- Available cyanide
- Total distilled cyanide
- Total non-distilled cyanide

The only fully automated free cyanide method

Method	Description	Measurement
ASTM D 7237	FIA	Gas Diffusion-Amperometry

Direct colorimetry is not measuring free cyanide



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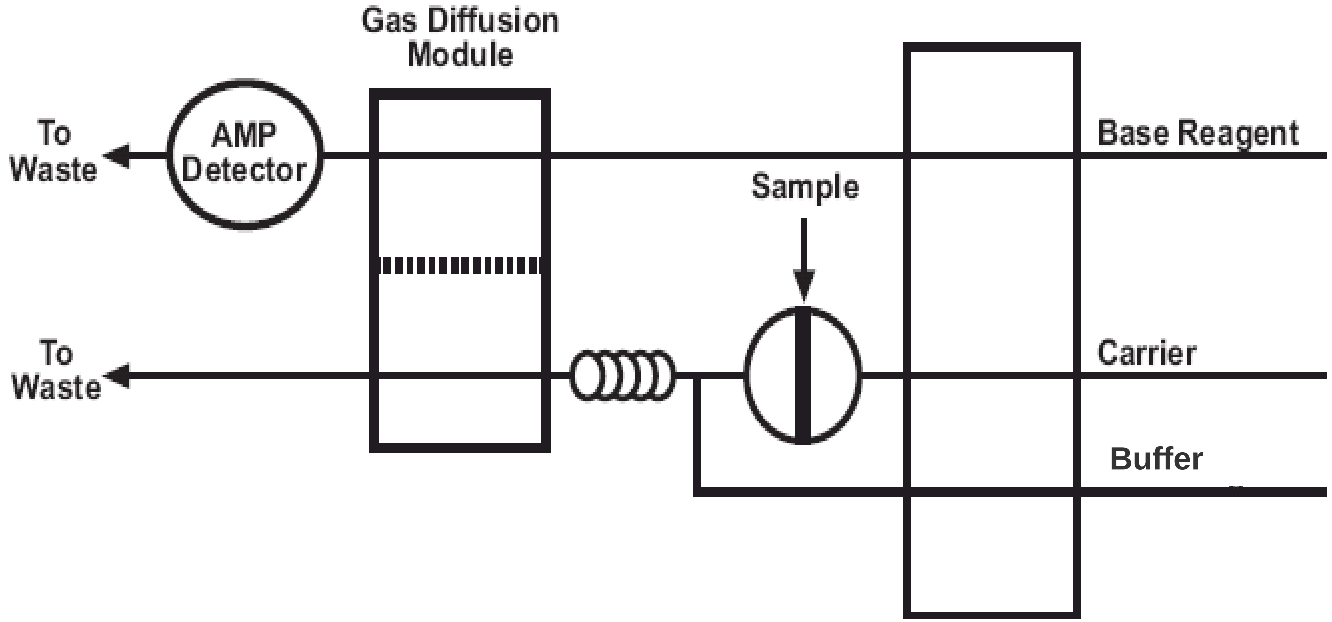
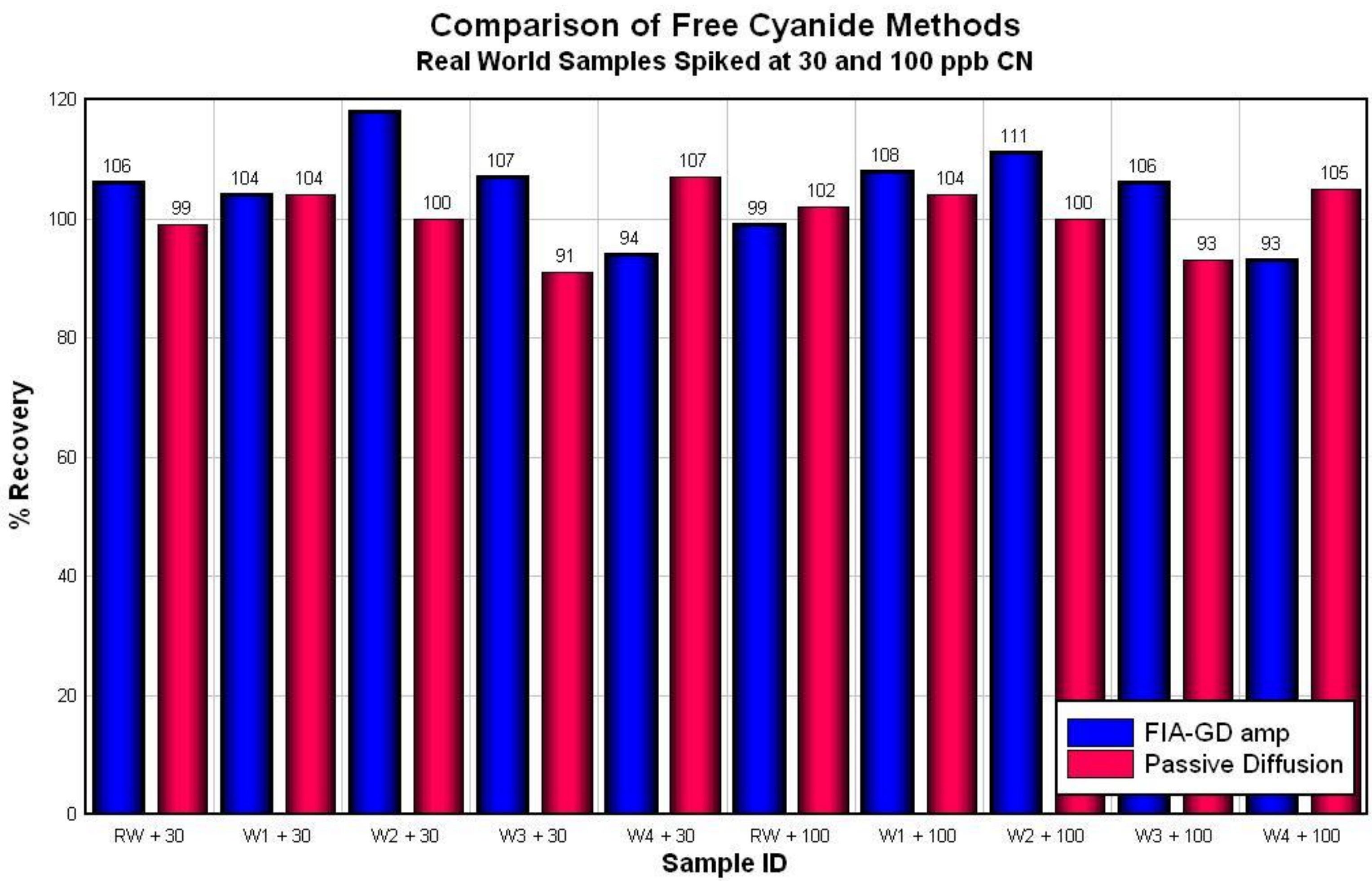
The free cyanide method by GD-amperometry



ASTM D7237-06

Real Data Comparison – Free CN



GD-amperometry methods for available cyanide – no CATC!

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

No distillation or pyridine required

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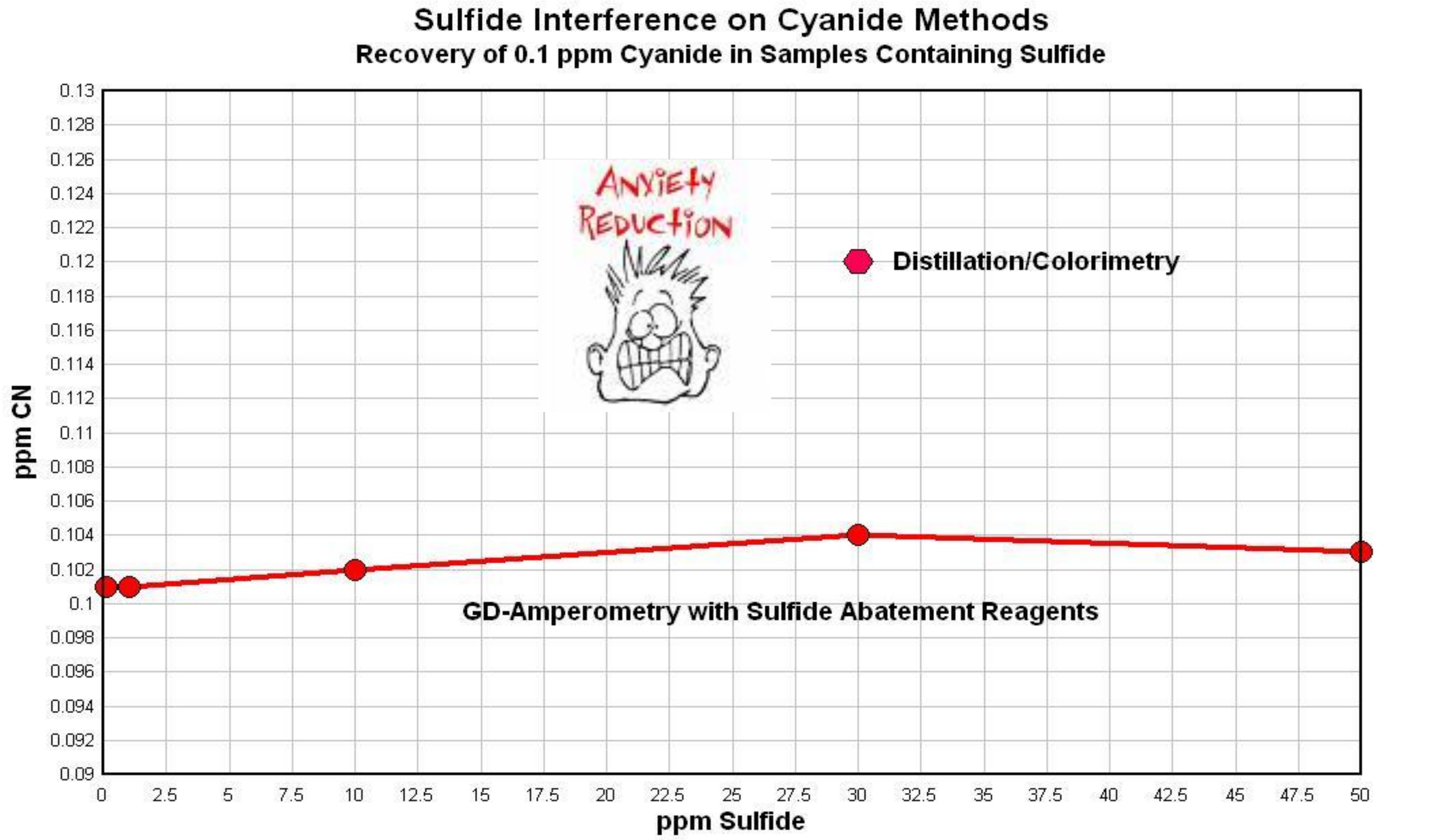
Sulfide does not interfere



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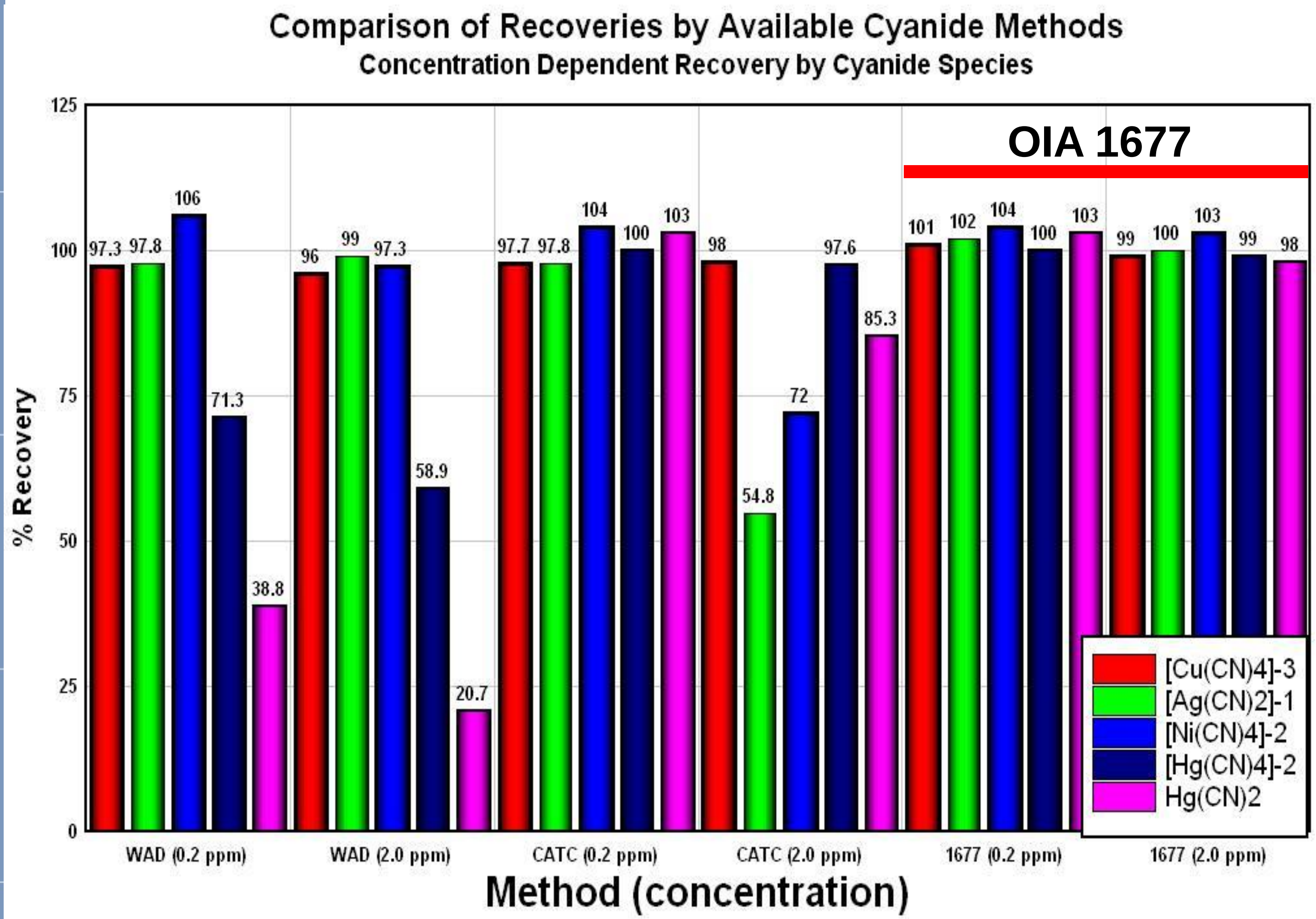
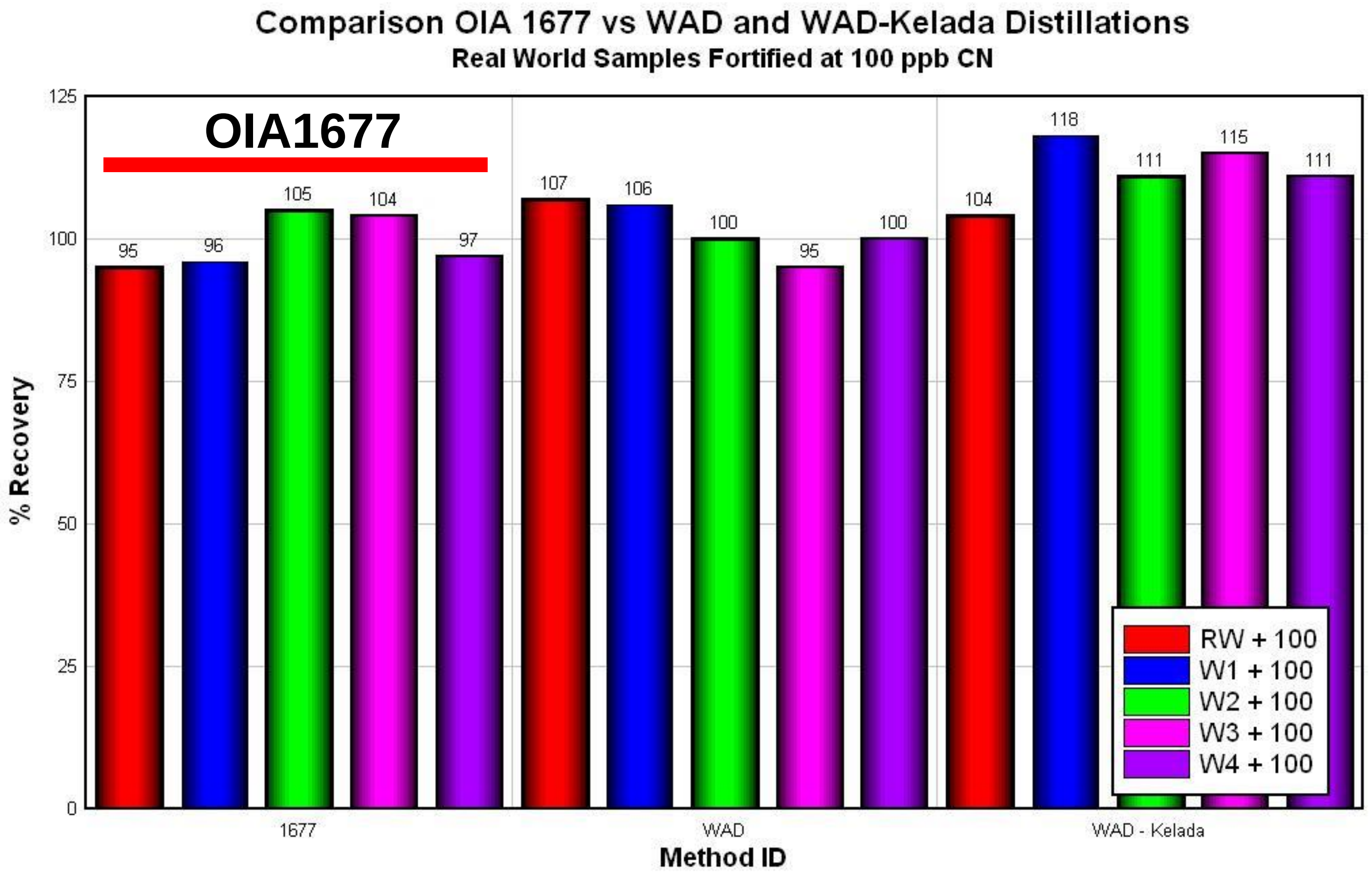
Quantitative recovery compared to other methods such as CATC



Precise and more accurate than WAD methods



GD-amperometry available CN has 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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GD-amperometry available CN saves time and labor

	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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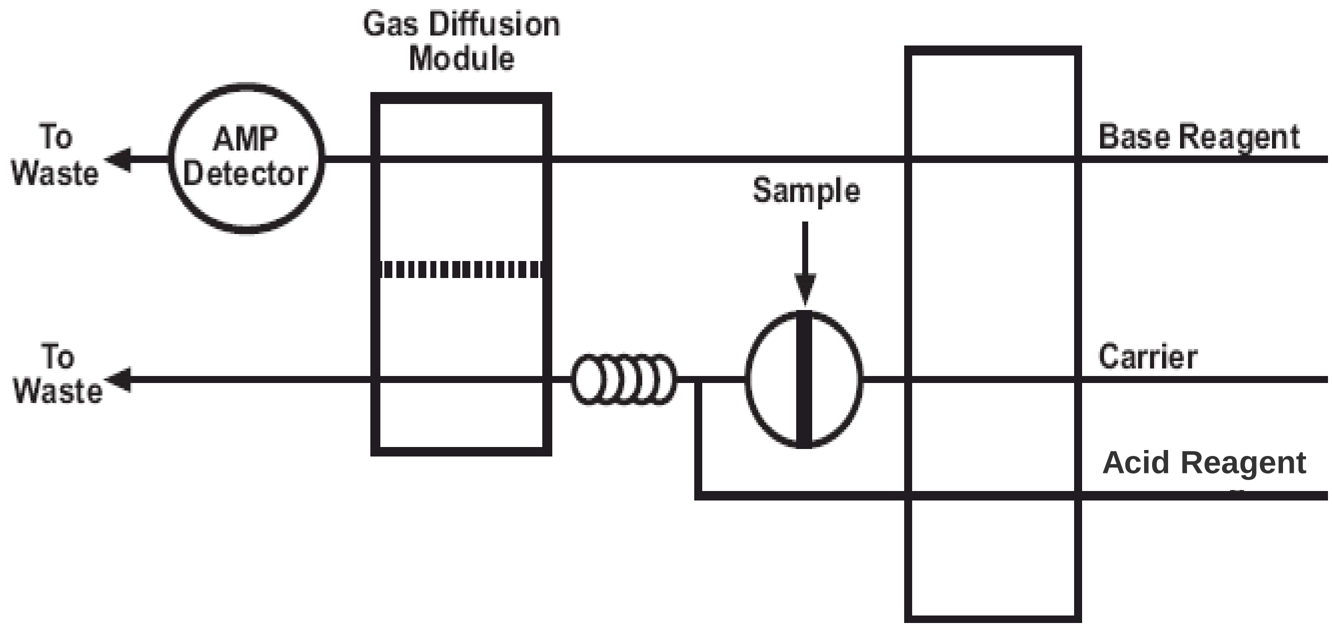
Less manipulation means better Available CN data

- No distillation
- 0.5 ppb MDL
- Up to 90 samples per hour
- Ease of Operation
- Very simple chemistry

Easy to use, understand, and environmentally friendly

No pyridine



OIA 1677, ASTM D6888-04 or ASTM D7284-08

Total cyanide methods using manual distillation

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

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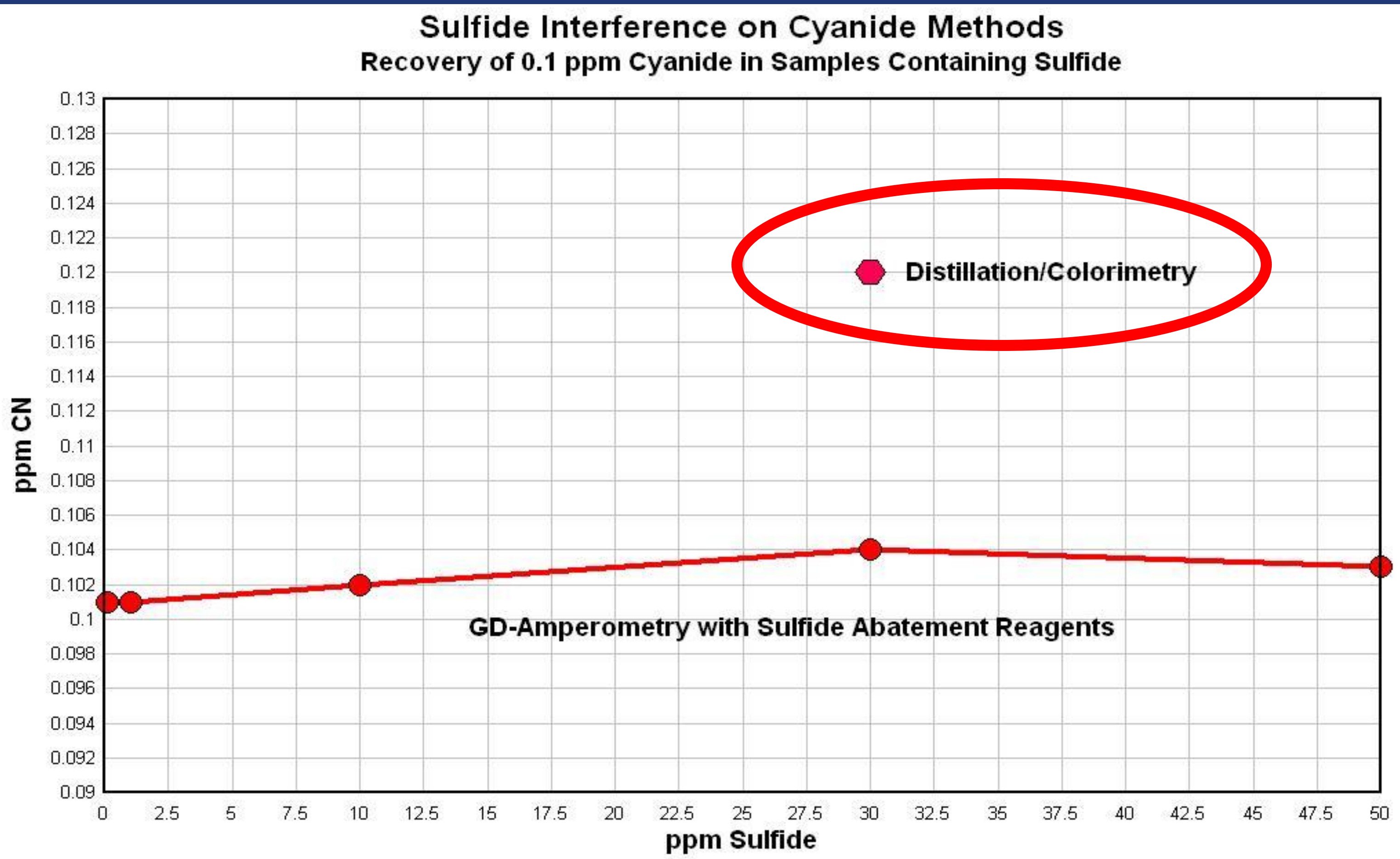
Most total cyanide analyses are by EPA 335.4 or similar

- Manual distillation
- Prolonged heating (125 °C) , strong acid (pH <2)
- Purging into basic absorber solution
- Colorimetry

ASTM D7284 manual distillation GD-amperometry method

- Distill samples
- Use GD-amperometry
- No pyridine
- Fewer interferences

Once again, sulfide does not interfere with GD-amperometry



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But wait, I thought distillation was bad?

Comparison of Measurements with Interferences Present

Sample (Total CN)	EPA 335.4	ASTM D7284
20 ppb	18.7	18.4
20 ppb +SCN + NO_3	227	229
200 ppb + SO_3	147	159
200 ppb + Ascorbate	152	154
200 ppb + Ascorbate + Ammonia	73	71
200 ppb + Ascorbate + Ammonia + OCL^-	47	49

What exactly do “total” cyanide methods measure?

- Iron Cyanide + Available CN

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

Comparison of Kelada and ASTM D7511-09

	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 %

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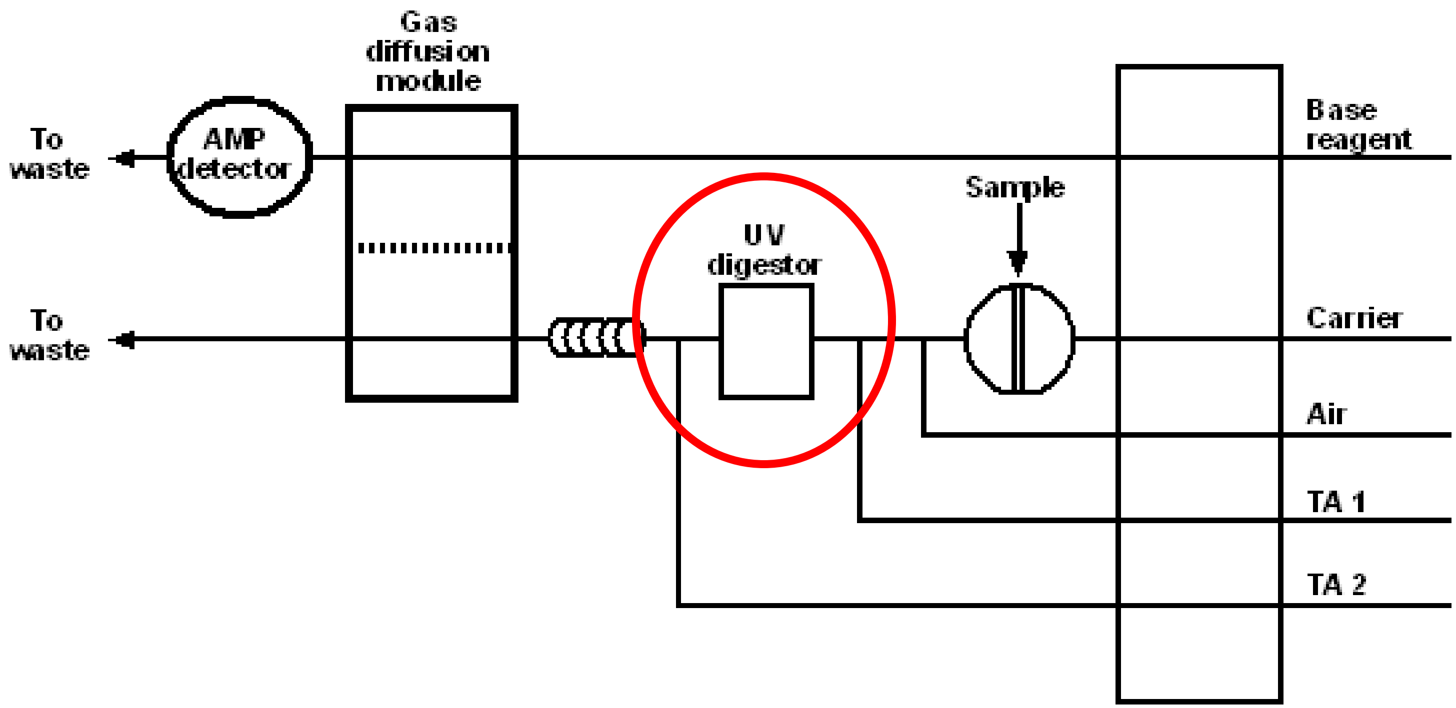
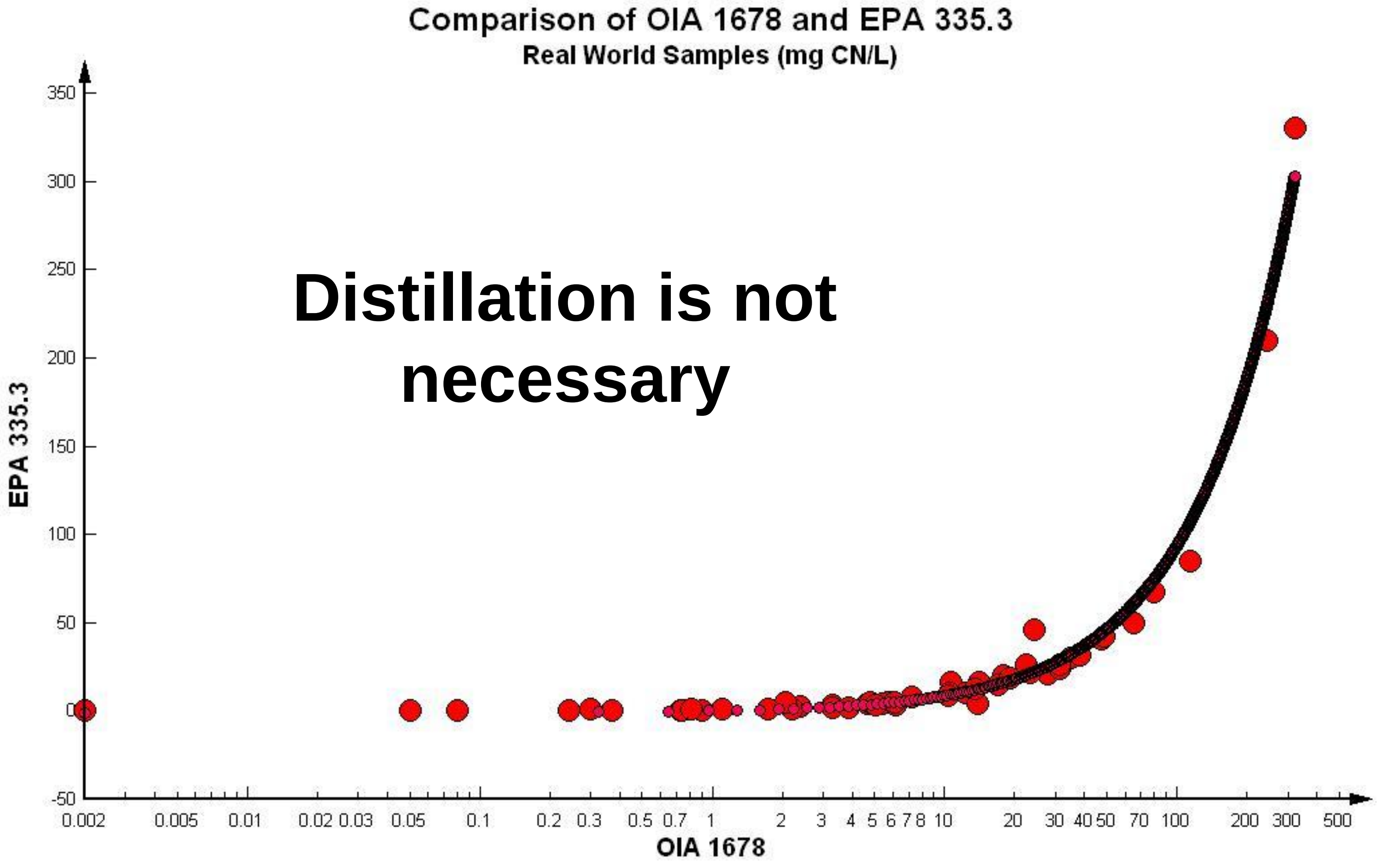
For total cyanide, simply add UV irradiation to the GD method

No pyridine



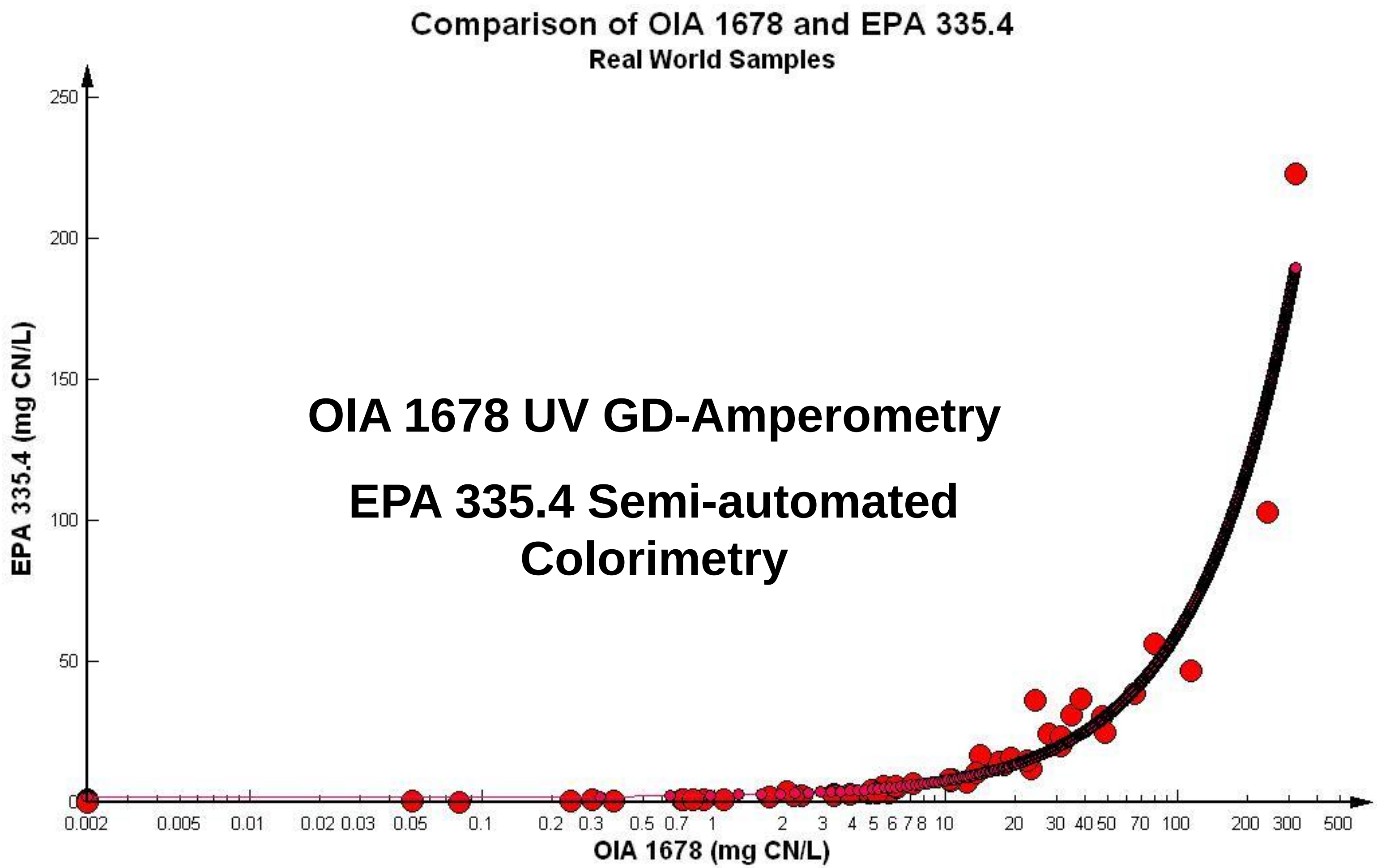
OIA1678 / ASTM D7511-09

Same results with and without flash distillation

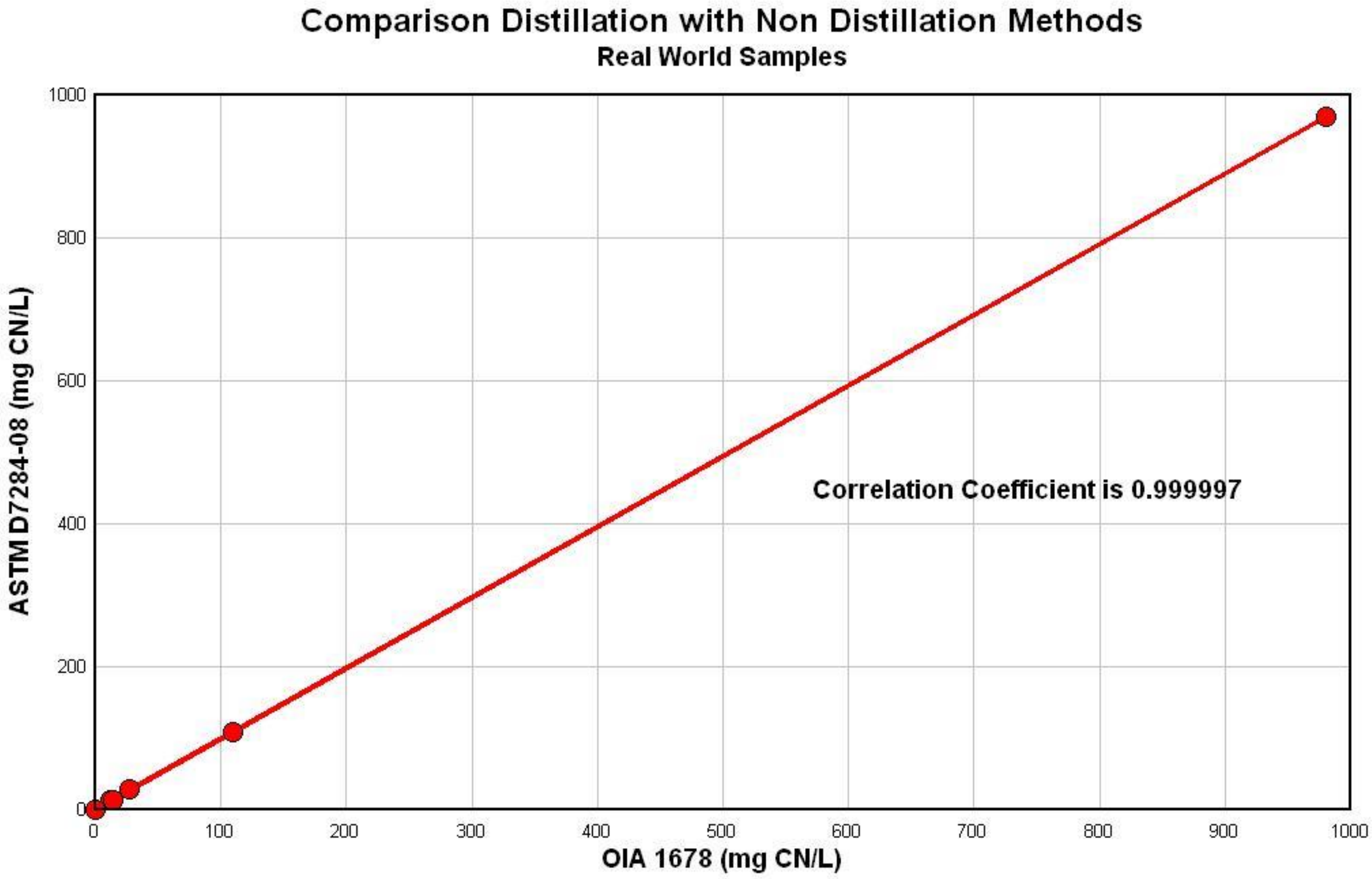


Distillation is not necessary

Same, but more precise results as manual distillation



ASTM D7511 and D7284 get the same result if no interferences



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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

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In summary, distillation/colorimetry should be replaced