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Three new Cyanide Methods at Standard Methods Part 4000

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August 2021


Well, there you go
again

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Contents

- Why do we need them at SM?
- Fundamental CN Chemistry
- **Sampling and Sample Preservation**
- Methods and Interferences
- Conclusion

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Why do we need these new methods at Standard Methods?

- **Greater acceptance of Standard Methods for the Examination of Water and Wastewater methods than for ASTM methods**
  - Standard methods requires methods be published elsewhere prior to publishing in Standard Methods
    - Working to change this
  - These methods are published and independently validated at ASTM and by ISO
  - Publication in SM should get wider acceptance nationally and globally

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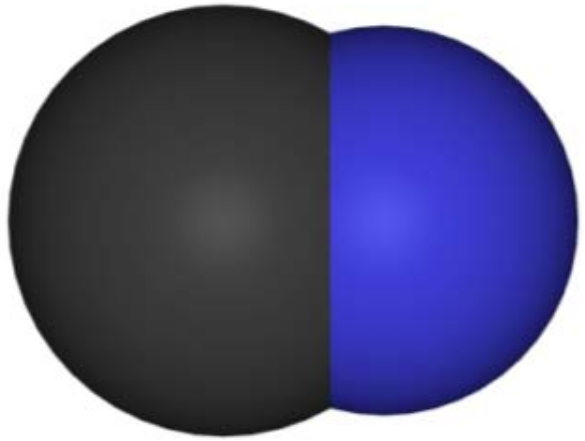
A generalized summary of cyanide and it's metal – cyanide species

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



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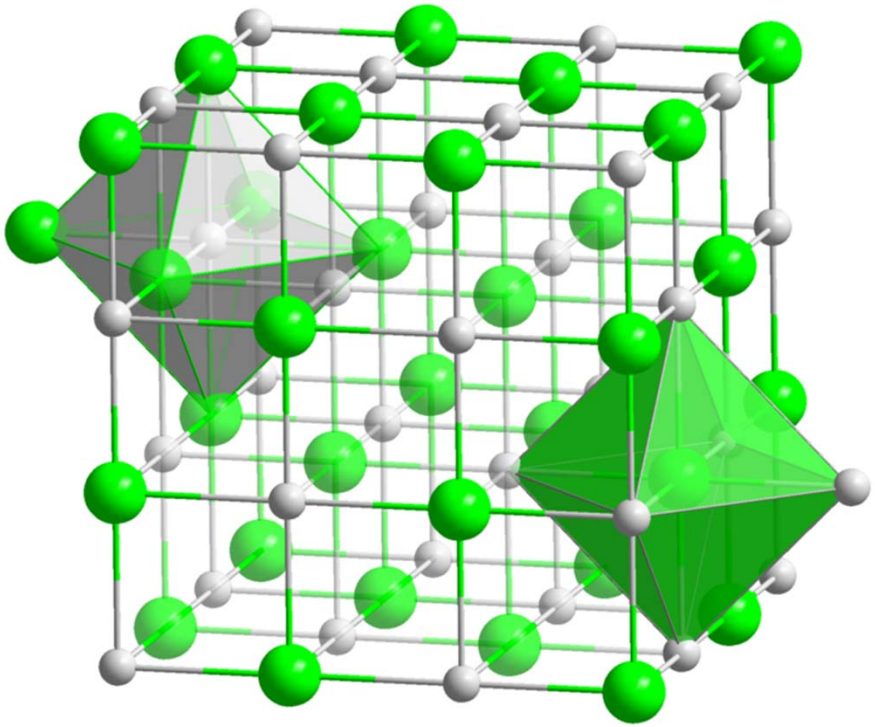
Alkali and alkaline earth metals form water soluble salts with the cyanide anion



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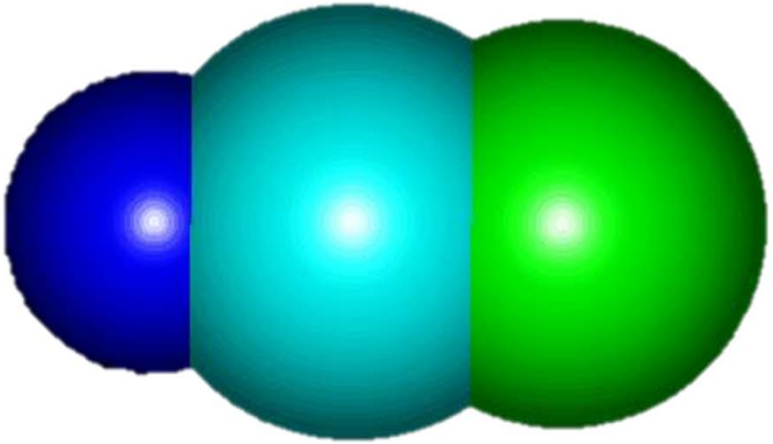
Get your free cyanide here. Hurry



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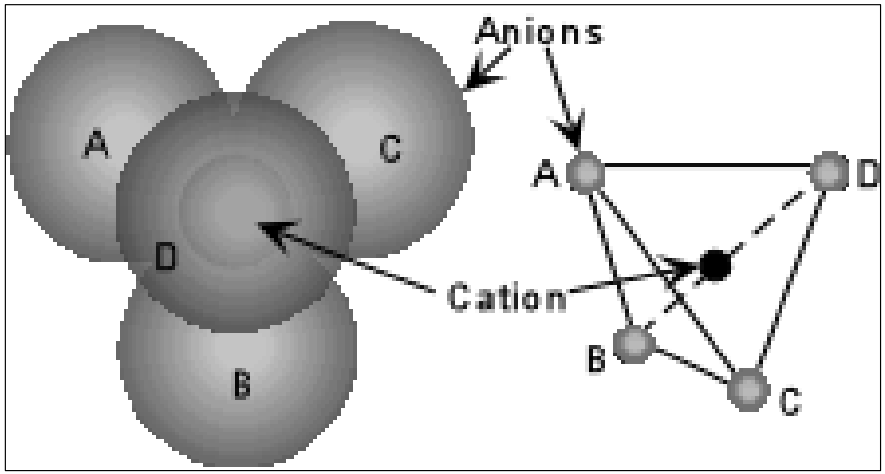
A tetragonal coordination complex anion with CN ligands



Zn, Cd, Cu, Ni, Hg

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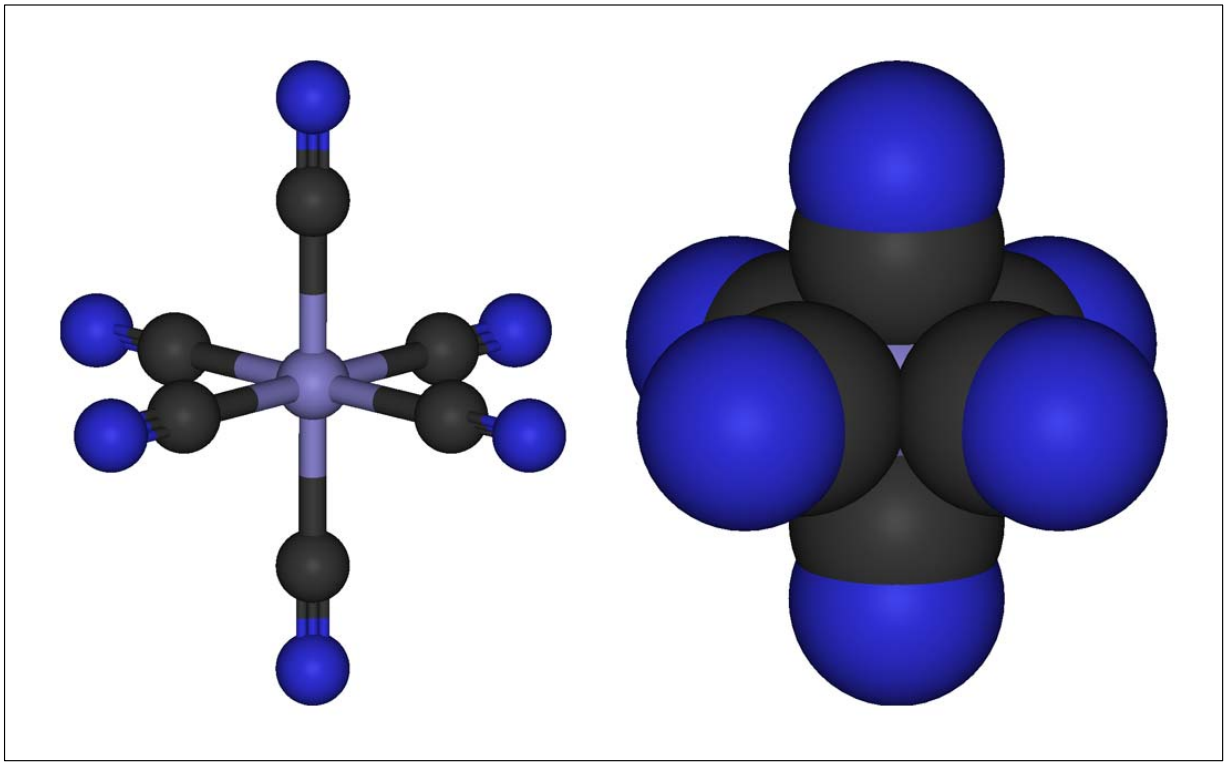
Iron and Cobalt CN are hexagonal coordination complexes with CN ligands



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Bonds between the metal and cyanide are moderate to strong

$[Hg(CN)_4]^{-2}$	
$[Cd(CN)_4]^{-2}$	Weak
$[Zn(CN)_4]^{-2}$	
$[Ag(CN)_2]^{-}$	
$[Cu(CN)_4]^{-3}$	
$[Ni(CN)_4]^{-2}$	Moderate
$Hg(CN)_2$	
$[Fe(CN)_6]^{-4}$	
$[Fe(CN)_6]^{-3}$	Strong
$[Co(CN)_6]^{-3}$	

$[Hg(CN)_4]^{-2} \rightarrow Hg(CN)_2 + 2CN^-$

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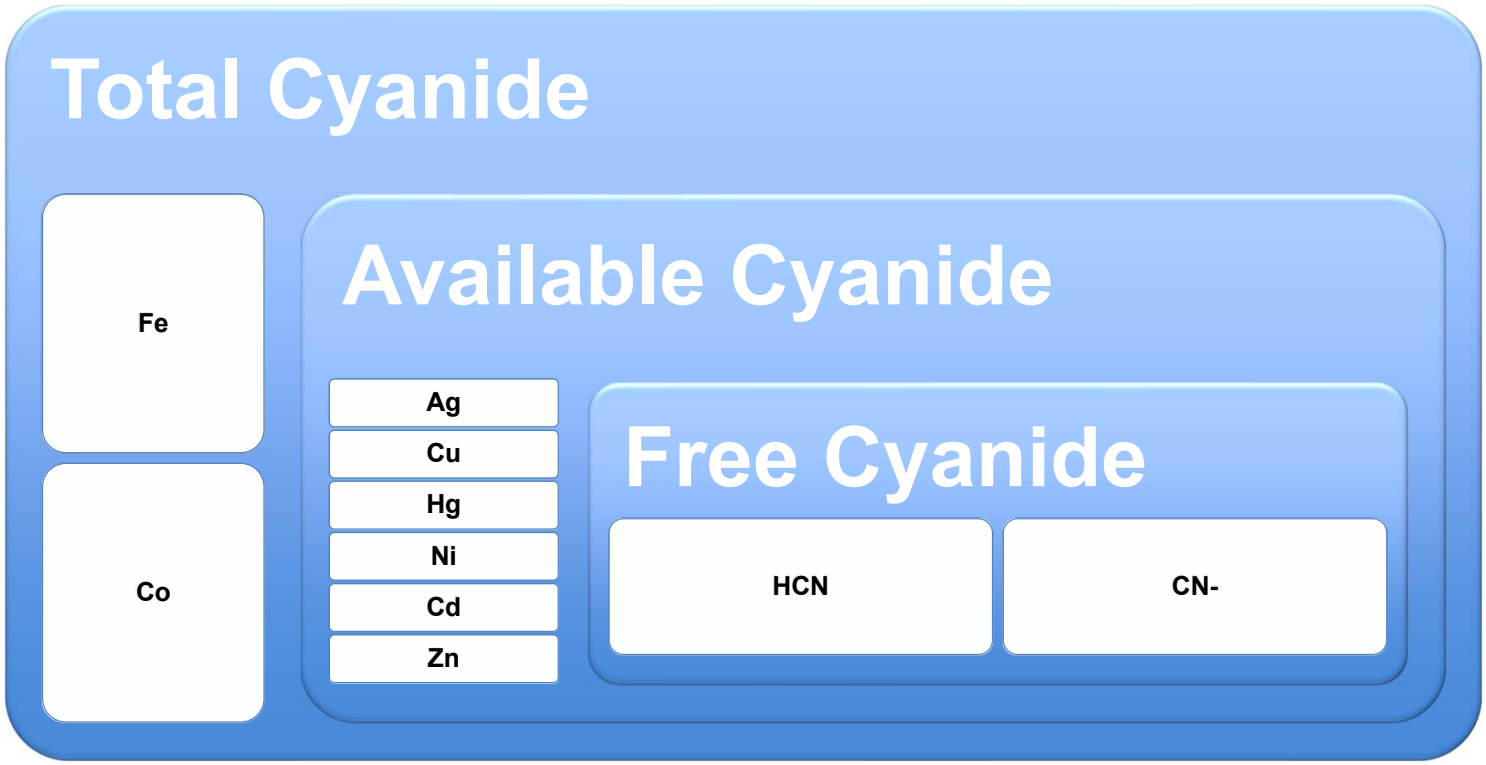
Cyanide methods measure the various cyanide “species” dissolved in water



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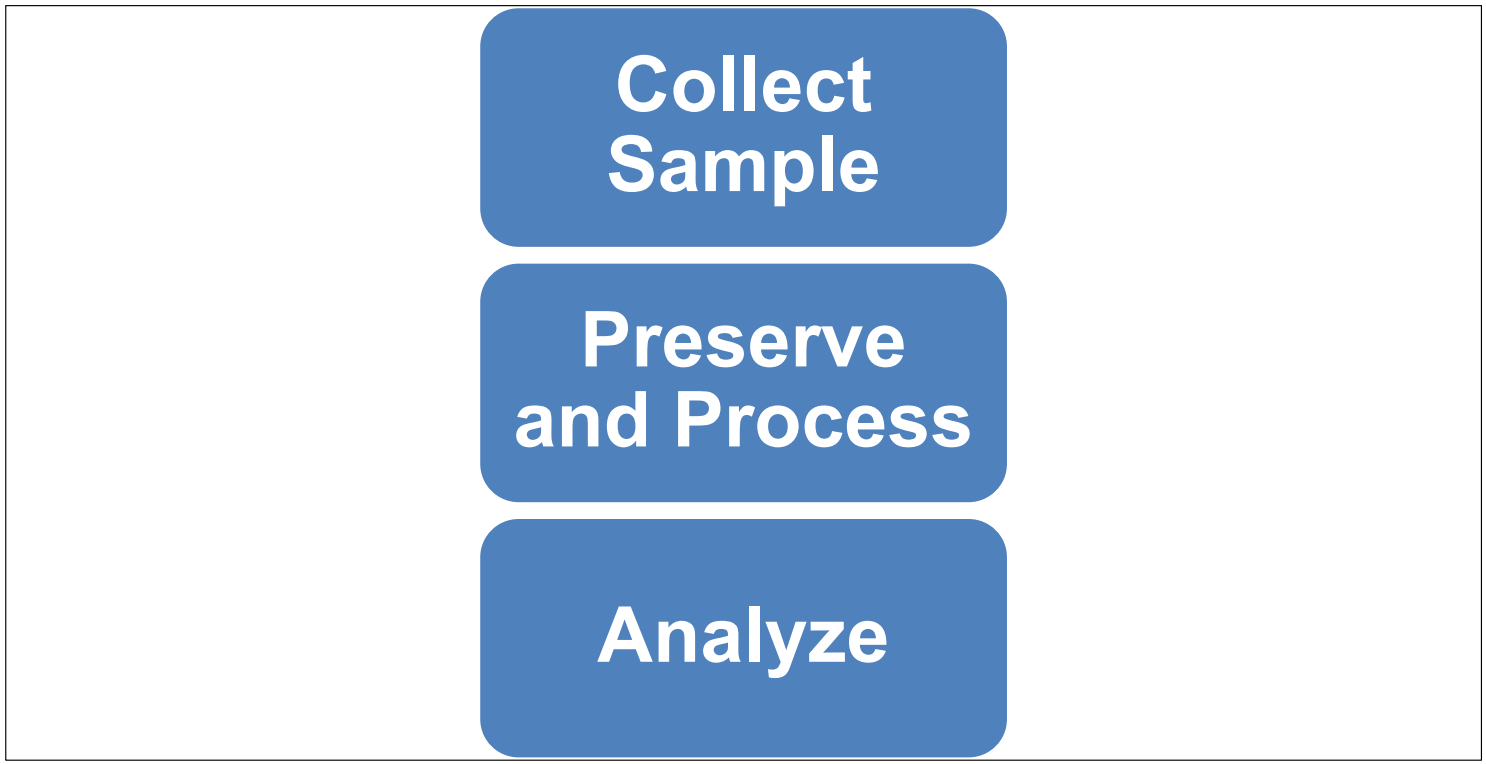
The new methods required revisions of 4500-CN Part A



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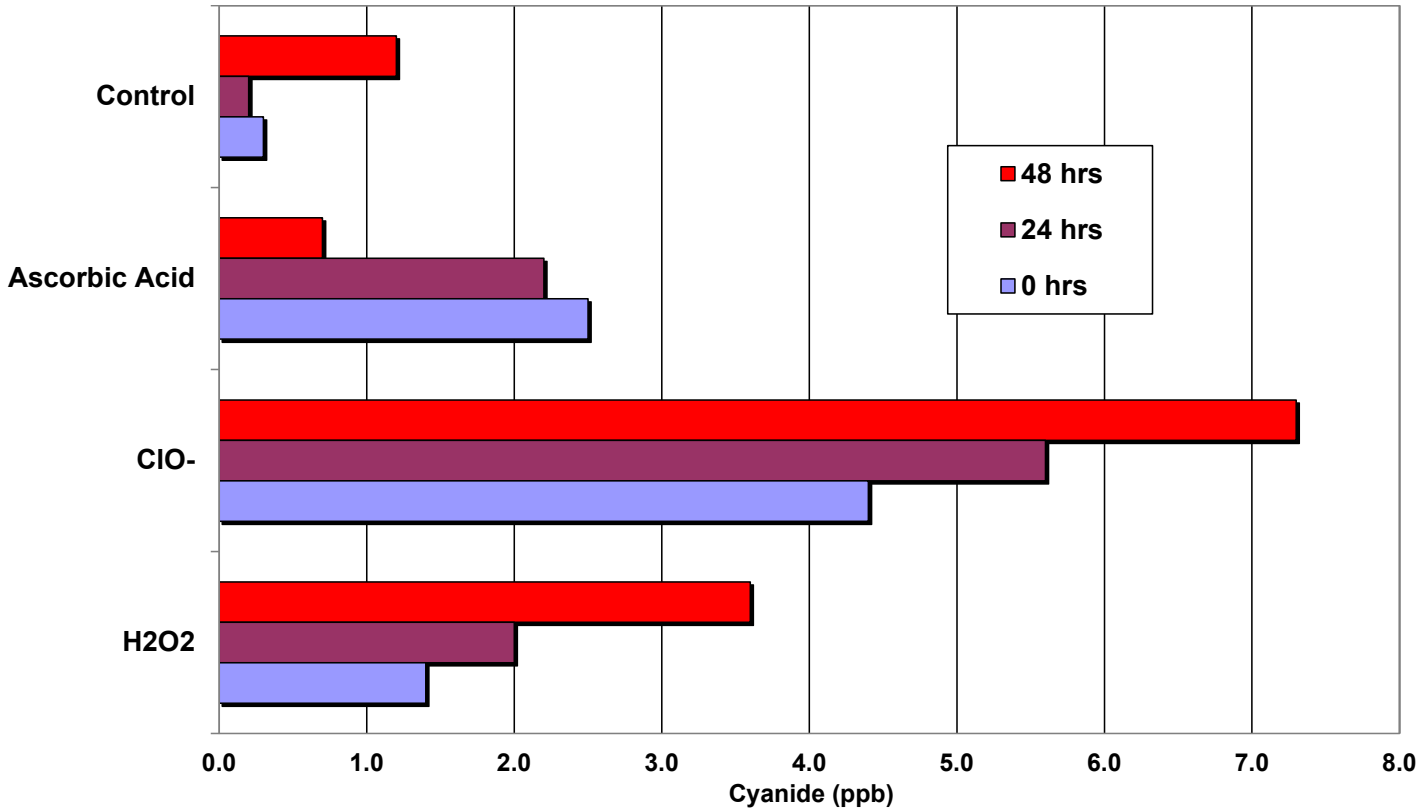
Cyanide formation after preservation at pH 12



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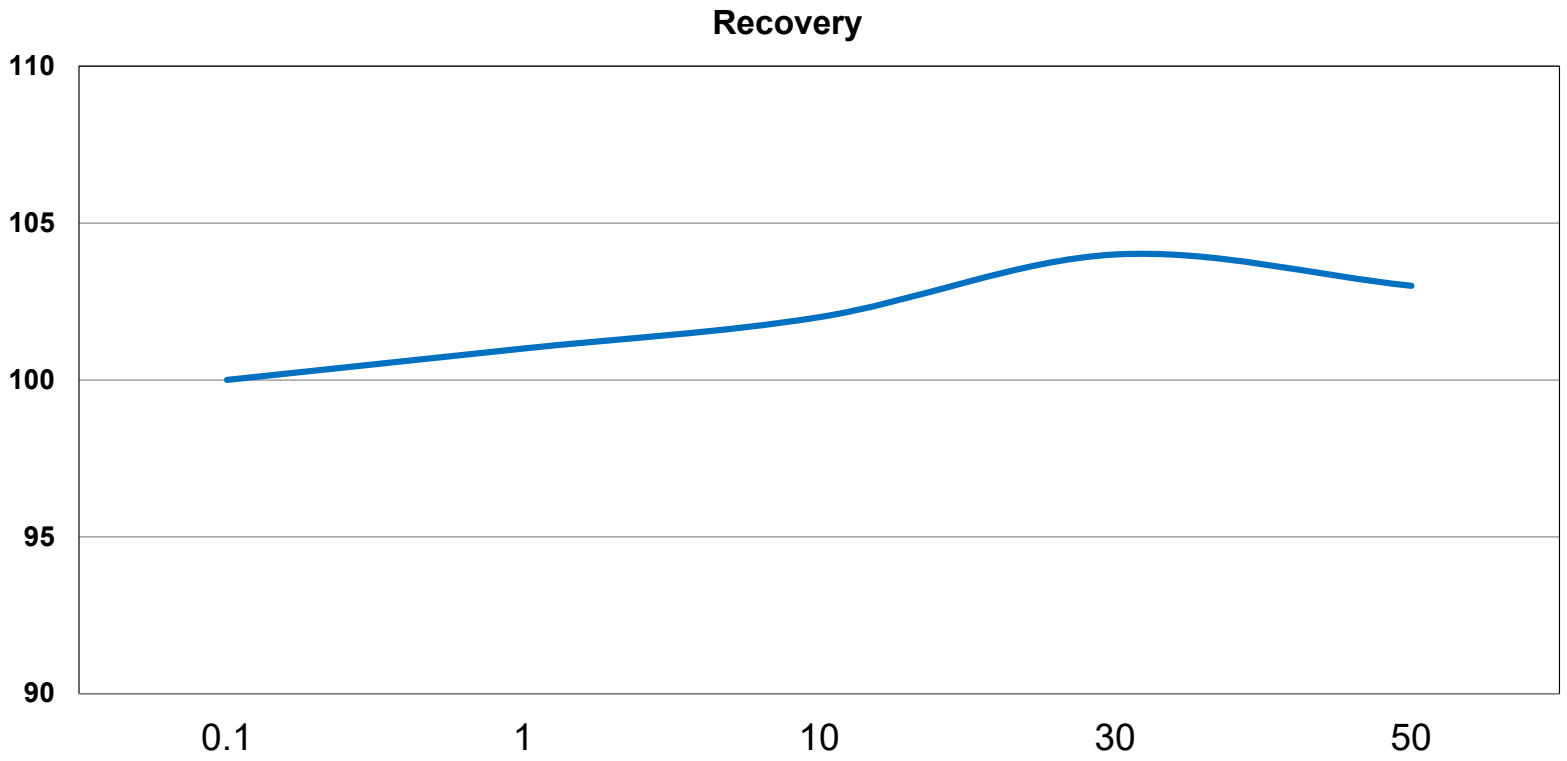
Recovery of 100 ppb CN in up to 50 ppm Sulfide using on-line sulfide abatement



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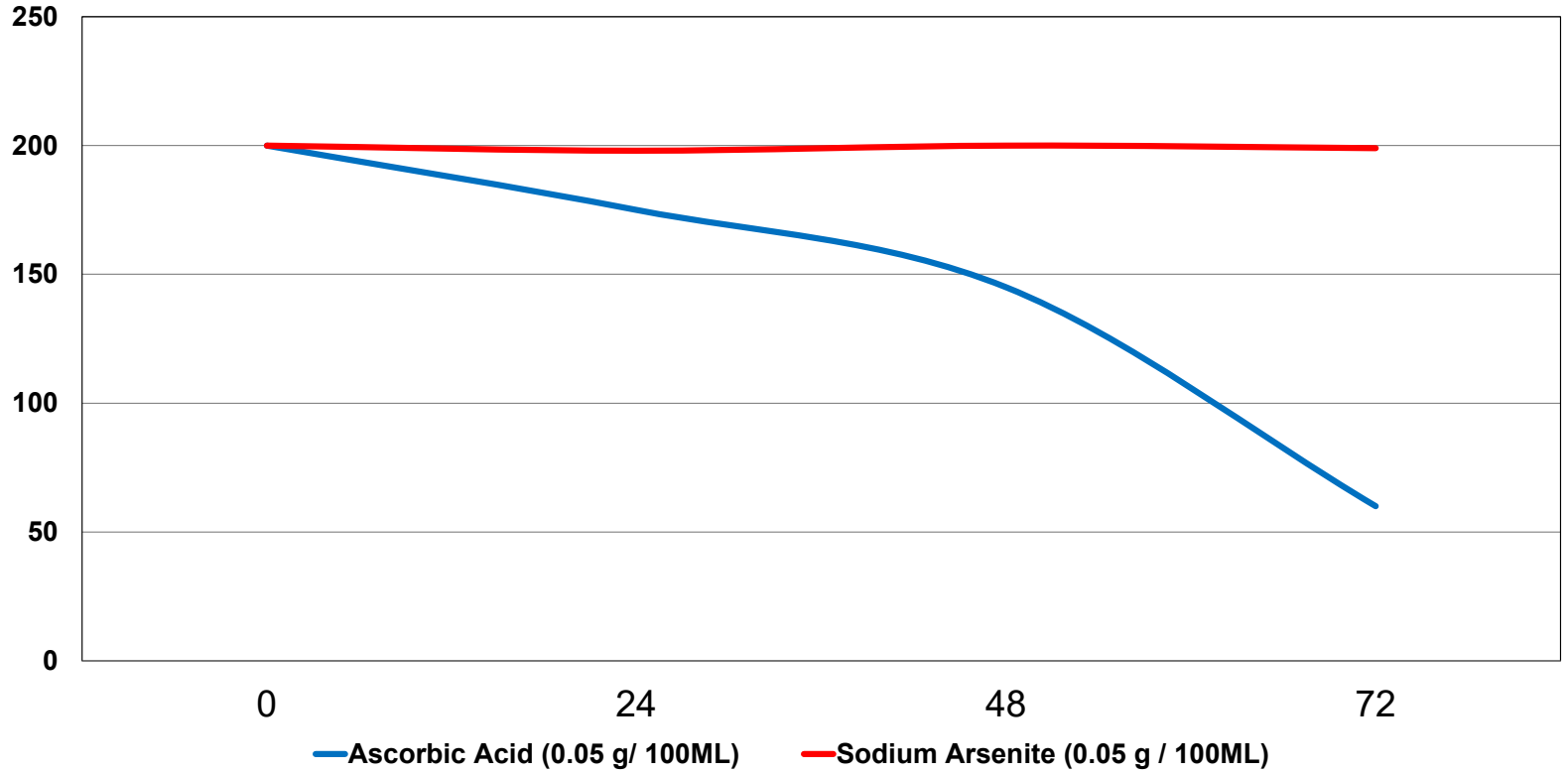
Loss of 200 ppb CN due to ascorbic acid addition



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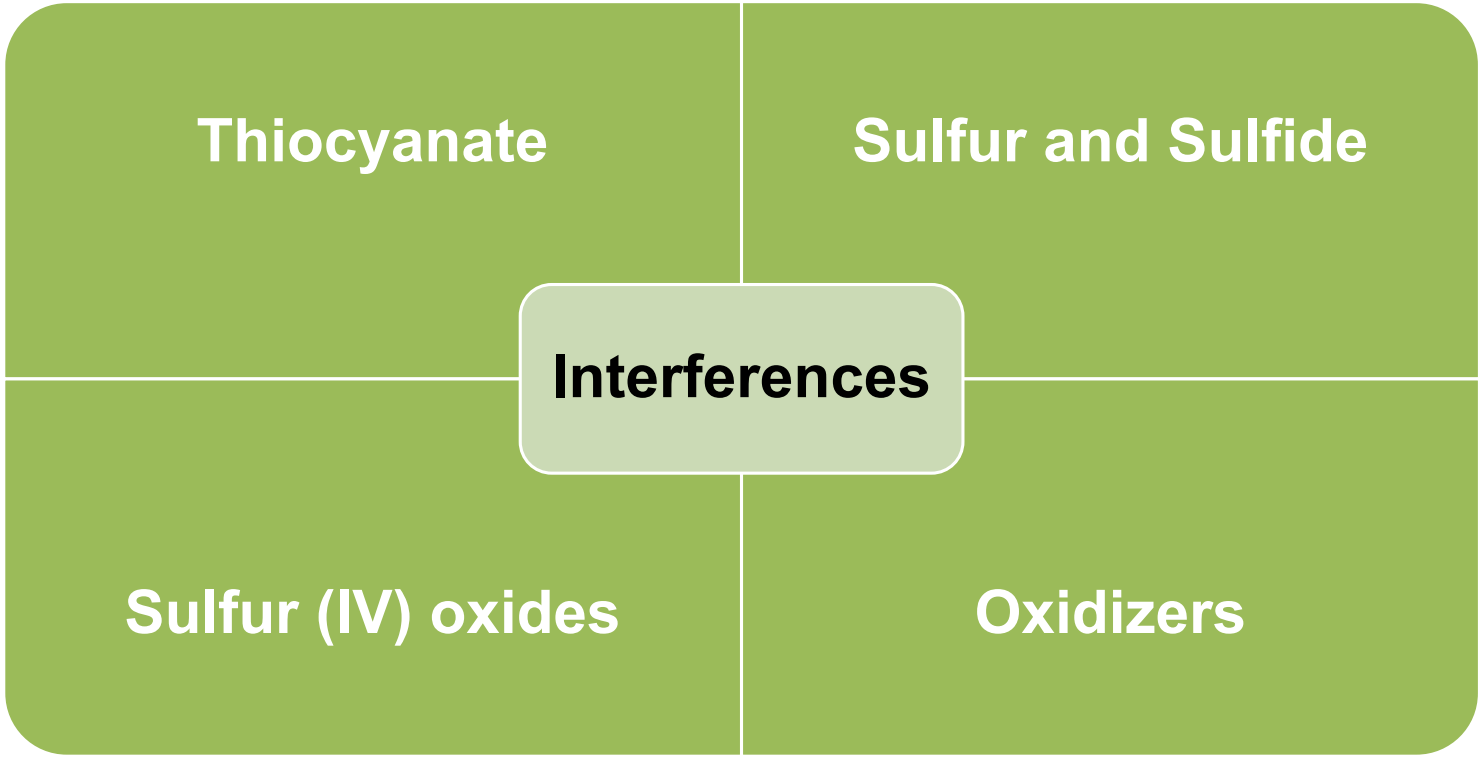
These compounds are in almost every sample and interfere significantly



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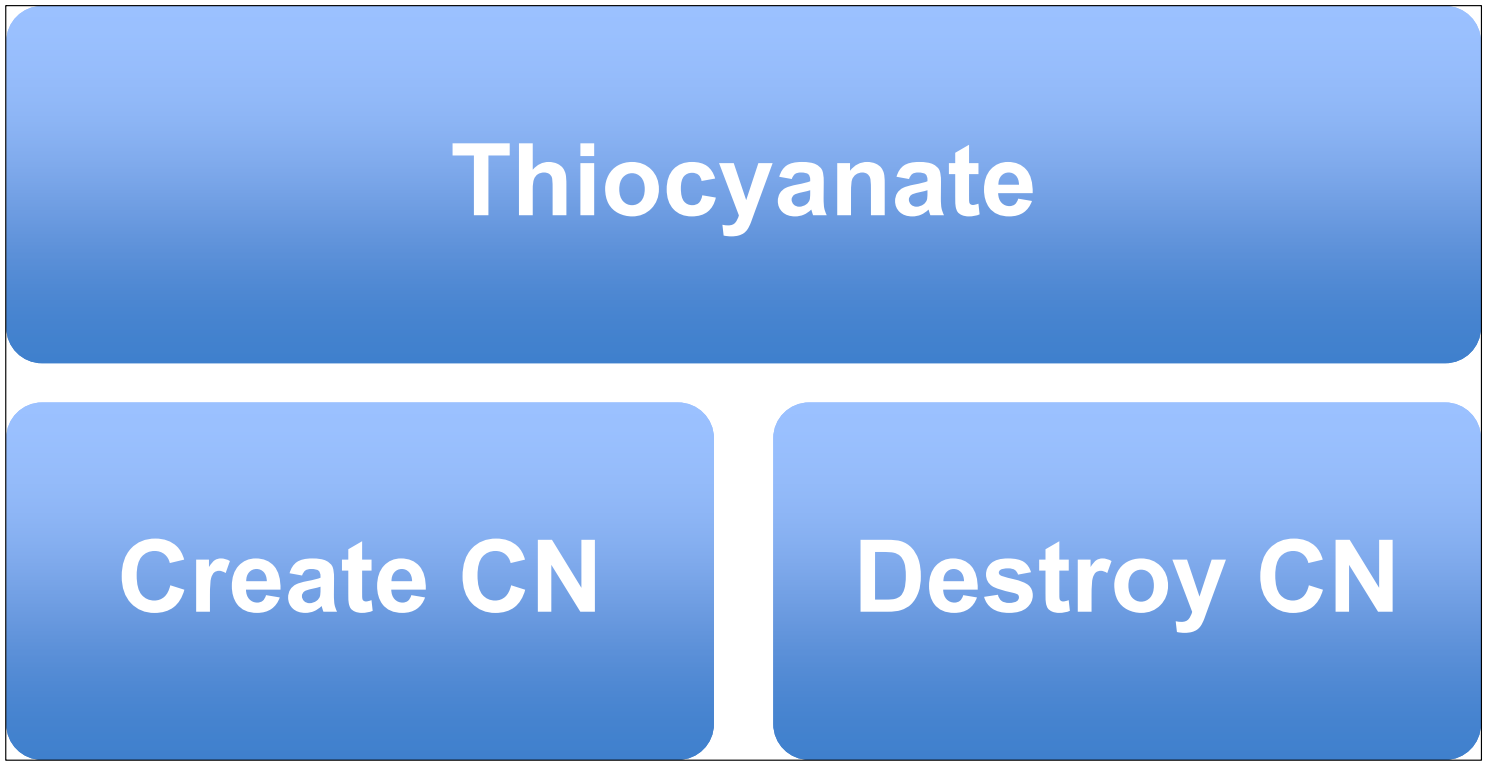
Thiocyanate causes both negative and positive interferences, particularly with distillation or CATC



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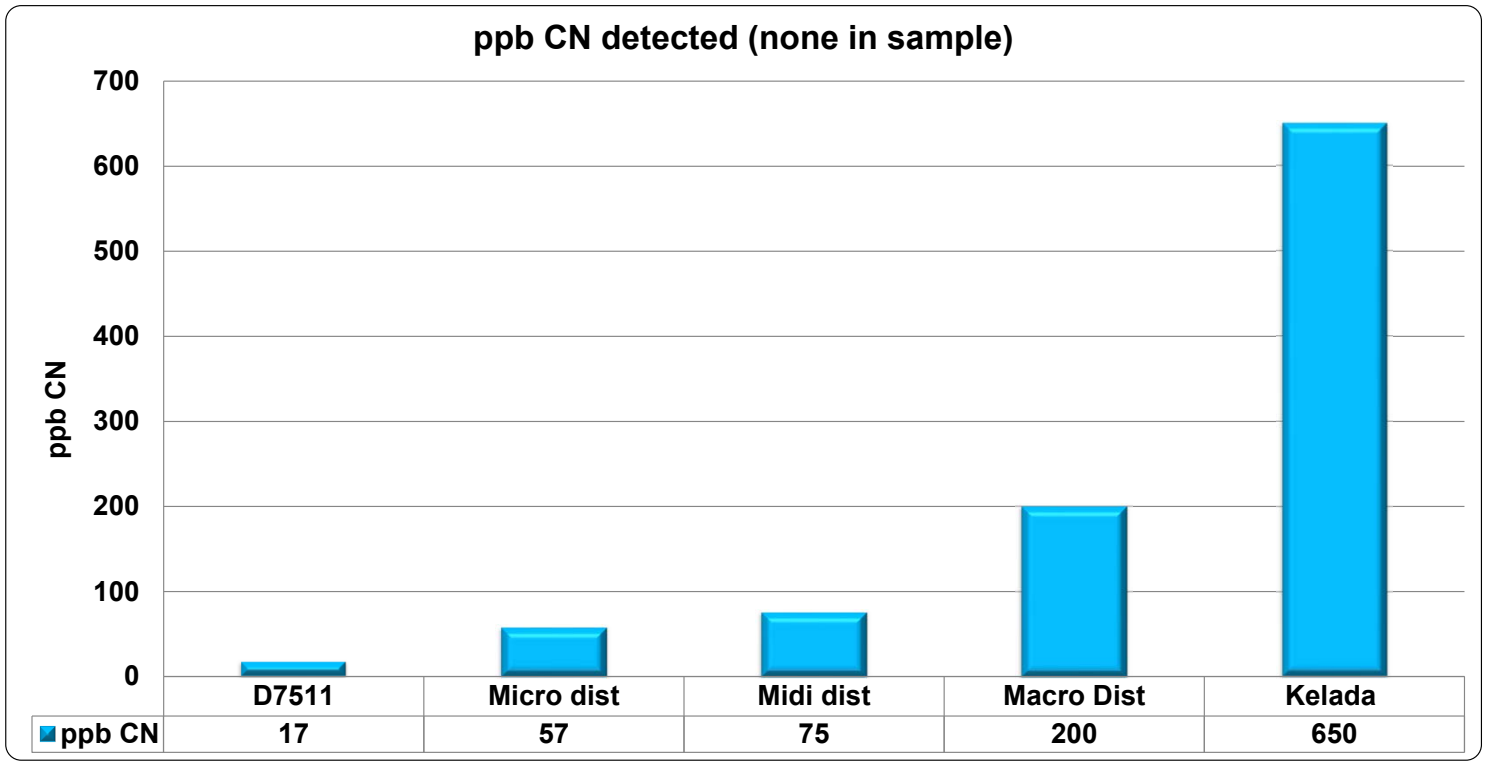
Recovery of CN from the ASTM “challenge matrix”



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Free Cyanide methods using gas diffusion

Method Number	Description	Measurement
ISO 20950-1:2018.	Micro-diffusion at pH 6	Amperometry
ASTM D7237-18	Auto-diffusion at pH 6	Amperometry
SM 4500-CN R	Auto-diffusion at pH 6	Amperometry

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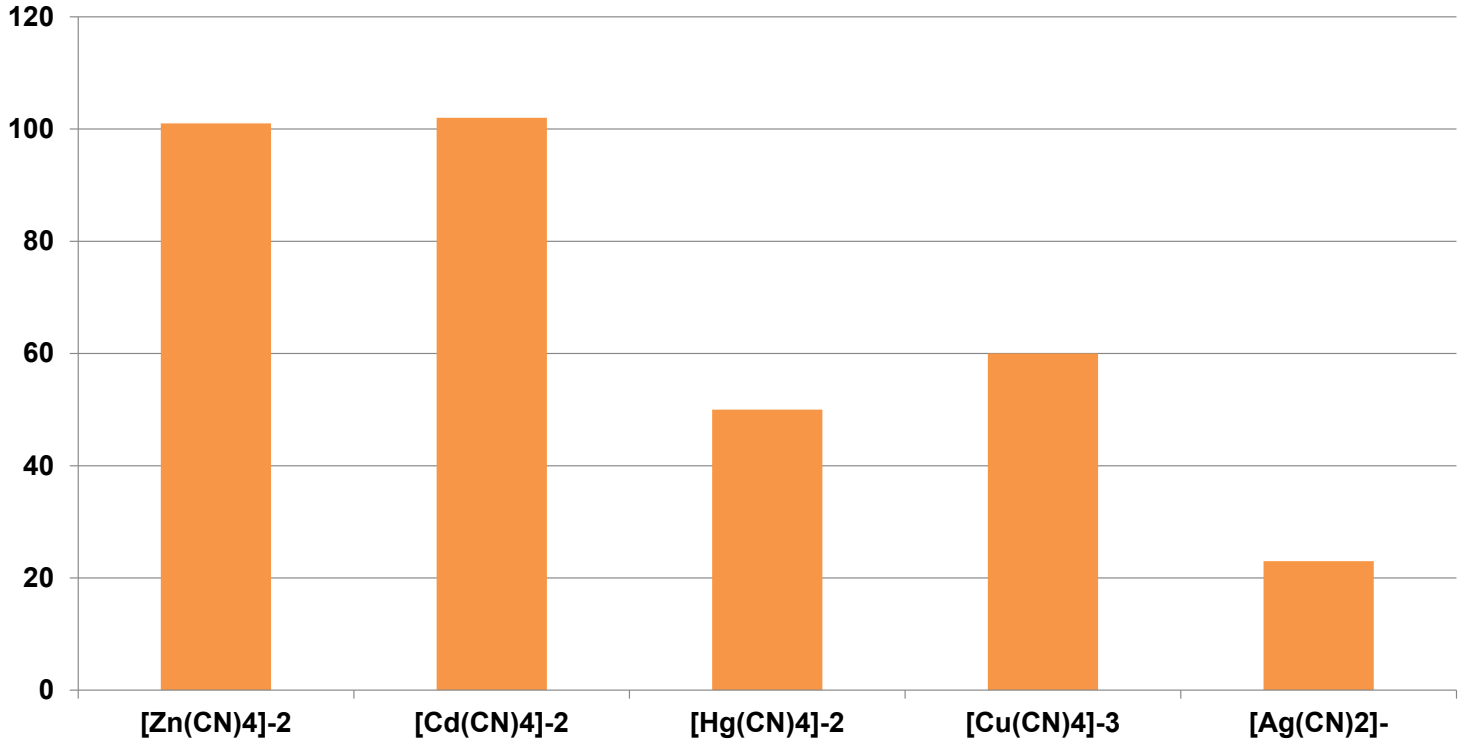
Recovery of metal-cyanide complexes by the free cyanide methods



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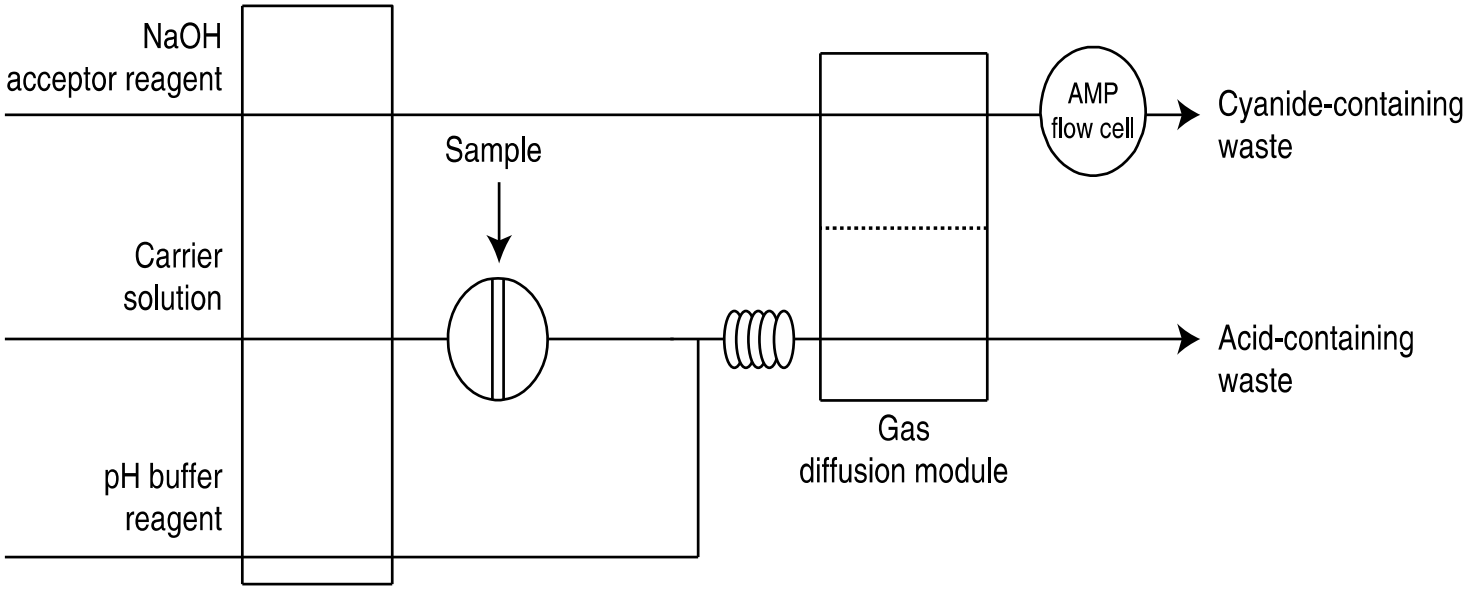
Free cyanide flow chemistry diagram



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Free Cyanide ASTM and ISO Data

Sample	Matrix[a]	*l*	*n*	*o*	*X*	$\bar{x}$	*η*	s_R	$C_{V,R}$	s_r
				%	µg/l	µg/l	%	µg/l	%	µ
1	Groundwater	11	22	8,33	822	815	99,1	60,9	7,47	8
2	Surface water	11	22	8,33	409	398	97,3	32,5	8,16	6
3	Potable water	11	22	8,33	195	202	104	16,0	7,92	1
4	Leach solution	11	22	8,33	167	179	93,3	12,8	7,15	2
5	Effluent	11	22	8,33	9,4	8,00	85,0	2,95	36,9	0

l number of laboratories after outlier rejection
n number of individual test results after outlier rejection
o percentage of outliers
X assigned value
$\bar{x}$ overall mean of results (without outliers)
η recovery rate
s_R reproducibility standard deviation
$C_{V,R}$ coefficient of variation of reproducibility
s_r repeatability standard deviation
$C_{V,r}$ coefficient of variation repeatability

[a] Origin of the samples:
Sample 1, spiked, Metallurgical Tailings Solution,
NevadaSample 2, spiked, Cherry Creek, Centennial,
Colorado Sample 3, spiked, Denver Aquifer, Parker,
Colorado
Sample 4, spiked, Heap Leach Drain Down Solution, Nevada
Sample 5, unspiked, Laboratory Treated Metallurgical Tailings Filtrate

Sample Number	Youden Pair 1		Youden Pair 2		Youc
	Sample 5	Sample 6	Sample 4	Sample 7	Sample 2
Number of retained values	8	8	8	8	8
True Concentration (C) ug/L	6.00	5.00	130	110	400
Mean Recovery (XBAR) ug/L	7.00	5.66	134	116	409
Percent Recovery	117	113	103	105	102
Overall standard deviation (S_T)	2.19	1.21	10.1	7.79	54.3
Overall relative standard deviation, %	31.3	21.4	7.54	6.72	13.3
Number of retained pairs	8		8		
Single operator standard deviation (S_o)	0.75		3.73		
Analyst relative standard deviation, %	11.8		2.92		

Biologically Treated Wastewater, Sample 8								
	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8
Single-operator								
Variance	0.04	0.58	1.05	7.23	2.17	30.5	4.64	0.02
Mean	65.3	58.5	55.4	69.8	76.7	61.6	55.2	71.1
Standard deviation (Sr or So)[A]	0.21	0.76	1.03	2.69	1.47	5.52	2.15	0.15
RSD, %	0.32	1.31	1.85	3.85	1.92	8.95	3.90	0.22
Interlaboratory								
Variance	62.0							
Std Dev of Mean	7.87							
Reproducibility SD (SR) or Total SD (ST)[B]	8.11							

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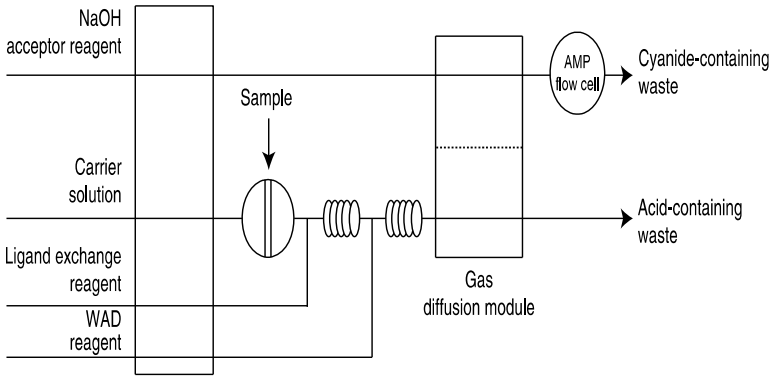
Ligand Exchange methods for available, or WAD cyanide

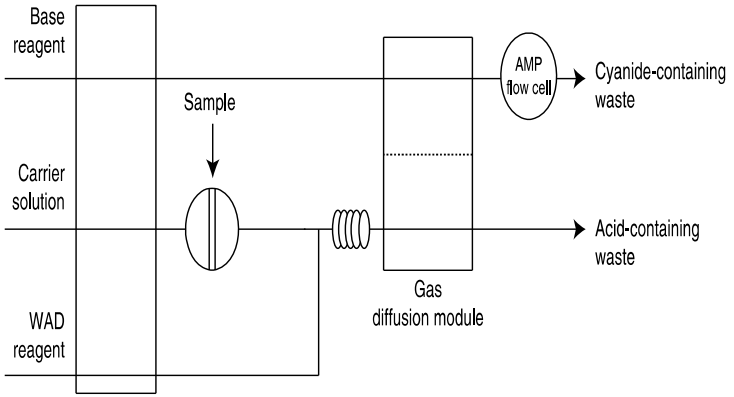
Method Number	Description	Measurement
OIA 1677	Ligand Exchange / Flow Injection Analysis	Gas Diffusion - Amperometry
ASTM D 6888	Ligand Exchange / Flow Injection Analysis	Gas Diffusion - Amperometry
ISO 20950-1:2018	Ligand Exchange / Flow Injection Analysis	Gas Diffusion - Amperometry
4500-CN Q	Ligand Exchange / Flow Injection Analysis	Gas Diffusion - Amperometry

Available cyanide (WAD) chemistry diagram

With automated ligand injection



Without automated ligand injection



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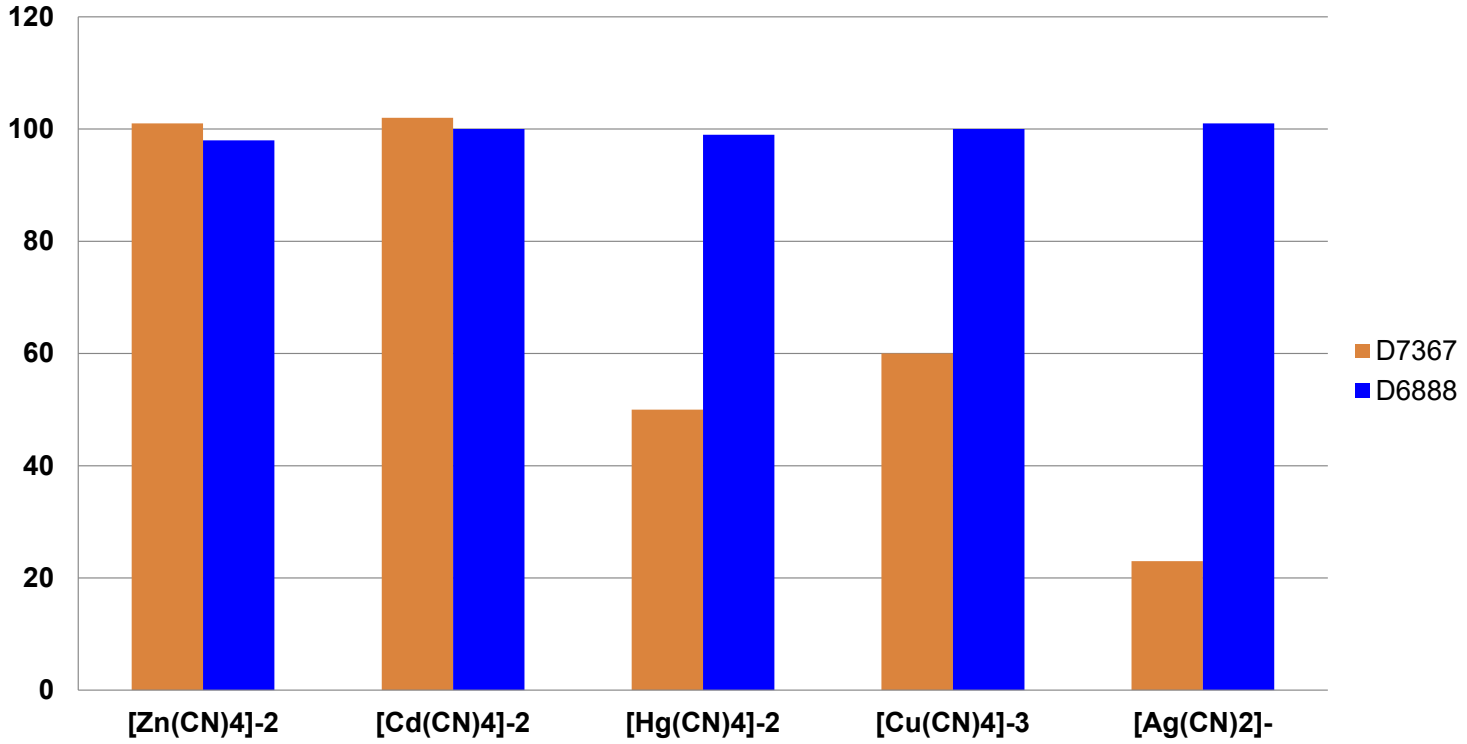
Recovery of metal-cyanide complexes by the free and available CN methods



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Summary of Data used for the available CN method

ISO data

Sample	Matrix	ι	n	o	X	X	η	SR	CV,R	sr
	Unit	each	each	%	µg/l	µg/l	%	µg/l	%	µg/l
1	Drinking water	8	36	20	9.52	9.31	98	1.29	13.6	0.285
2	Ground water	9	32	10	23.8	25.6	108	2.72	11.4	0.400
3	Surface water	10	40	9.1	238	240	101	25.5	10.7	2.67
	Unit	each	each	%	mg/l	mg/l	%	mg/l	%	mg/l
4	Tailings decant solution	11	44	0	0.566	0.535	95	0.083	14.7	0.004
5	Barren solution	11	44	0		30.1		4.00		0.331
6	Tailings Slurry Filtrate	11	44	0		96.9		6.06		0.991
7	Leach Slurry Filtrate	9	36	18.2		1161		74.1		12.2

l	number of laboratories after outlier rejection
n	number of individual test results after outlier rejection
o	percentage of outliers
X	assigned value
x	overall mean of results (without outliers)
η	recovery rate
SR	reproducibility standard deviation
CV,R	coefficient of variation of reproducibility
sr	repeatability standard deviation
CV,r	coefficient of variation repeatability

ASTM Data

Sample Location	Sample	Number of Measure-ments	Assigned Concentration of WADCN (mg/L)	Mean, WADCN (mg/L)	Overall Standard Deviation (mg/L)	Relative Standard Deviation (%)	Interlaboratory Repro-ducibility (mg/L)	Interlaboratory Repro-ducibility (%)
Synthetic wastewater	AC 19721	8	0.008	0.0071	0.0082	102.5	0.0213	267
Synthetic wastewater	AC 19723	8	0.009	0.0083	0.0046	51.1	0.0120	133
Synthetic wastewater	AC 19726	8	0.070	0.064	0.006	8.6	0.0156	22.3
Synthetic wastewater	AC 19722	8	0.080	0.0072	0.0097	12.1	0.0252	32
Synthetic wastewater	AC 19724	8	0.300	0.266	0.024	8.0	0.0624	20.8
Synthetic wastewater	AC 19725	8	0.350	0.315	0.027	7.7	0.0020	0.6

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Total Cyanide non-distillation methods

Method Number	Description	Measurement
ASTM D7511-12	Segmented flow injection, UV irradiation	Gas Diffusion - Amperometry
ISO 22066:2020	Segmented flow injection, UV irradiation	Gas Diffusion - Amperometry
4500-CN P	Segmented flow injection, UV irradiation	Gas Diffusion - Amperometry

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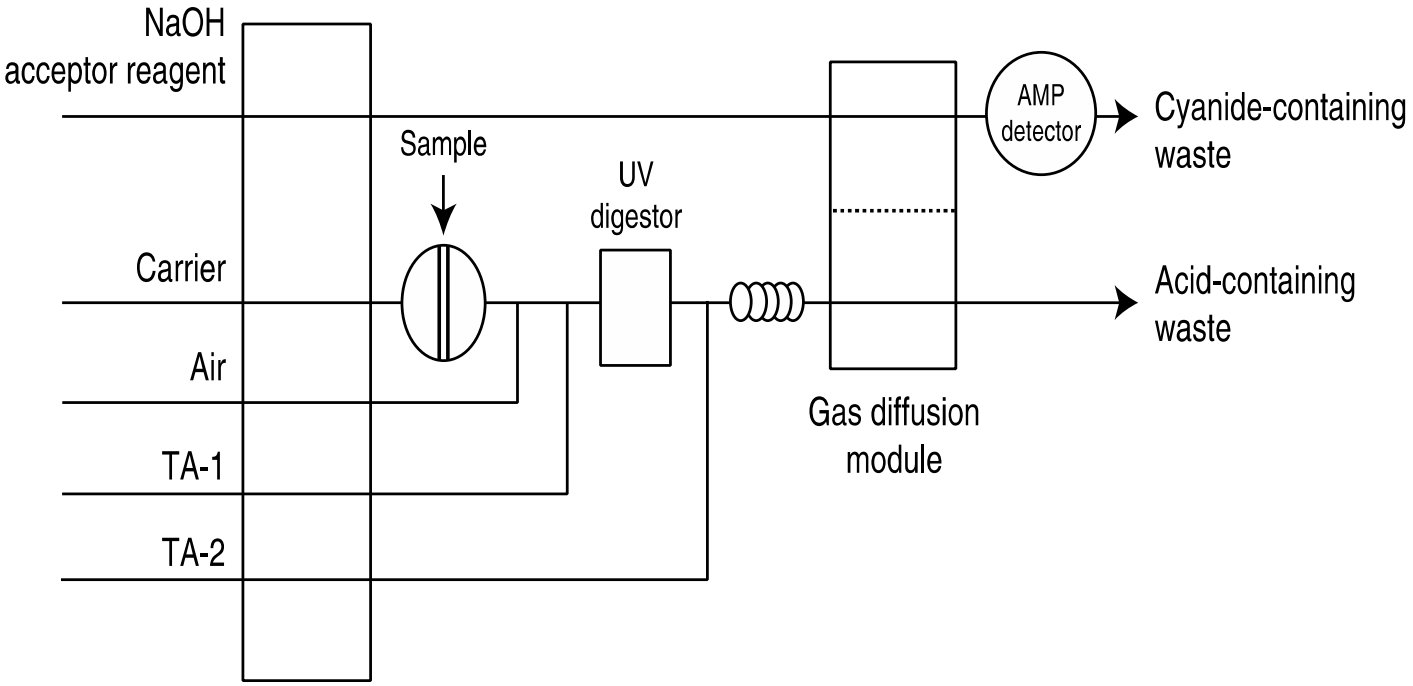
Total cyanide analysis chemistry flow diagram



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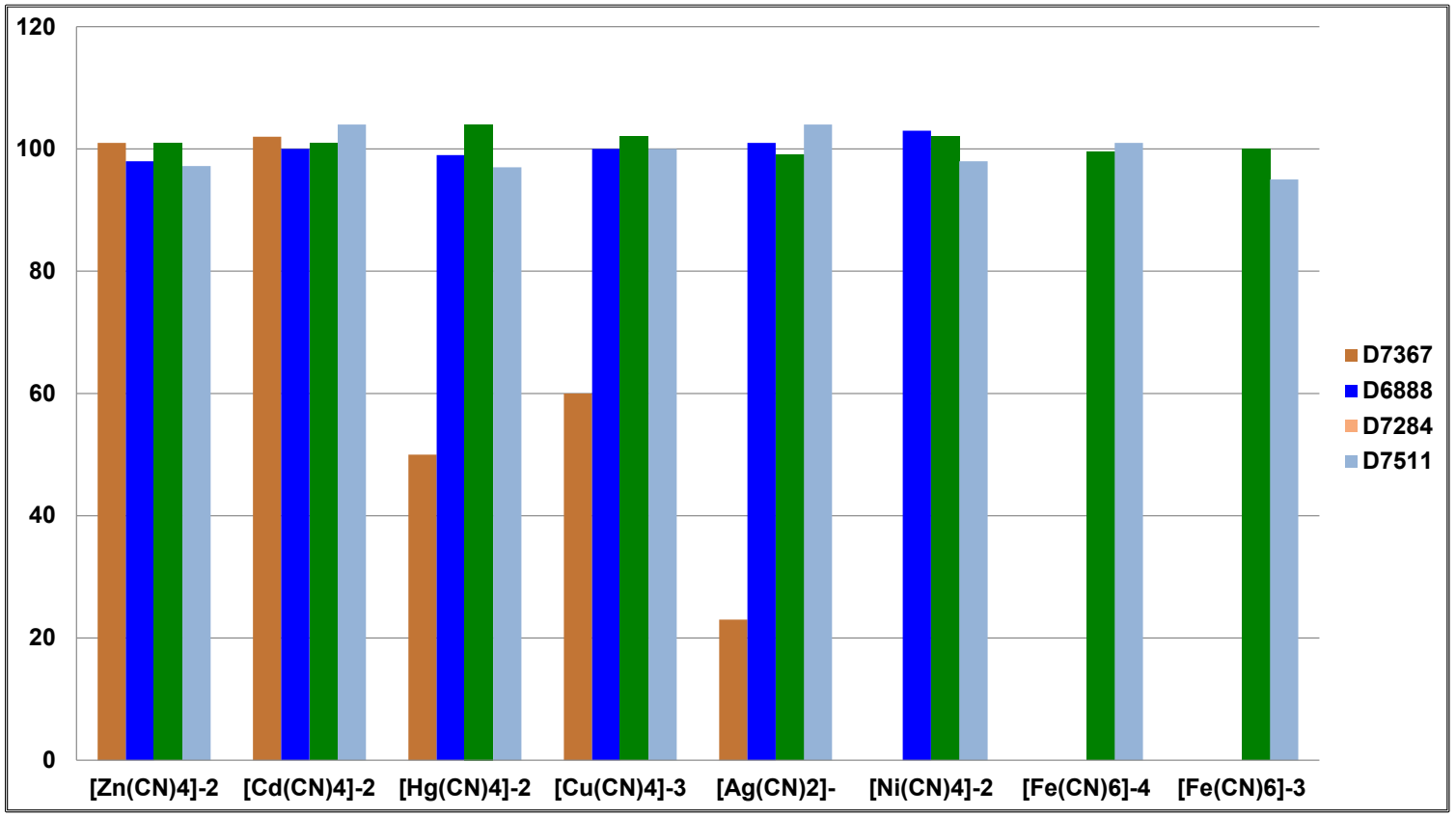
Recovery of metal-cyanide complexes by ASTM D7237, D6888, D7284 and D7511 (equivalent to new SM method)



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Summary of data used for the total cyanide method

Sample	Matrix[a]	l	n	o	X	$\bar{x}$	η	S_R	CV_iR	sr	CV_ir
				%	µg/ml	µg/ml	%	µg/ml	%	µg/ml	%
1	Drinking water	10	40	9,1	0,223	0,235	105	0,022 8	9,7	0,004 6	2,0
2	Ground water	10	50	9,1	0,025	0,027	110	0,003 2	11,9	0,000 9	3,4
3	Surface water	10	40	9,1	0,504	0,546	108	0,029	5,3	0,001	1,8
4	Tailings decant solution	10	40	9,1	-[b]	0,33		0,033	9,9	0,007 3	2,2
5	Heap Leach Barren	10	40	9,1	-[b]	0,145		0,033	22,6	24,1	1,9
6	Mill tailings slurry filtrate	10	40	9,1	1 262	1 309	104	138	9,8	24,4	1,9
7	Mill leach slurry filtrate	10	40	9,1	72,8	78,6	108	8,98	11,4	1,32	1,7

l	number of laboratories after outlier rejection
n	number of individual test results after outlier rejection
o	percentage of outliers
X	assigned value
$\bar{x}$	overall mean of results (without outliers)
η	recovery rate
S_R	reproducibility standard deviation
$C_{V,R}$	coefficient of variation of reproducibility
s_r	repeatability standard deviation
$C_{V,r}$	coefficient of variation of repeatability

[a] Origin of the samples:

Sample 1 Spiked, Denver Aquifer Exempt Domestic Well, Parker, Colorado.

Sample 2, Spiked, Alluvial-Dawson Dual Aquifer Exempt Domestic Well, Parker, Colorado.

Sample 3 Spiked, Cherry Creek, Centennial, Colorado.

Sample 4 Spiked Metallurgical Process Reclaim Solution, Winnemucca, Nevada.

Sample 5 Heap Leach Barren Solution, Carlin, Nevada.

Sample 6 Mill Tailings Slurry Filtrate Solution, Battle Mountain, Nevada.

Sample 7 Mill Leach Slurry Filtrate Solution, Battle Mountain, Nevada.

[b] Biased reference value.

Sample	#6	#9	#5	#7	#2	#8	#1	#4	#3
Number of values	24	24	24	21	21	21	21	21	21
True values (ug/L)	4.0	7.0	20.0	30.0	100	1030	2040	3450	4320
Mean	6.1	8.6	19.6	31.8	93.6	974	1850	2740	4320
% Recovery	153	123	97.8	107	93.6	94.5	90.5	79.5	95.4
Overall standard deviation	1.29	2.77	5.43	18.5	12.5	137	243	703	432
Overall % standard deviation	21	32	28	58[a]	13	14	13	26	11

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