Flow Solution™ FS 3700 Automated Chemistry Analyzer

Free Cyanide by Gas Diffusion and Amperometric Detection
ASTM D7237-10, Flow Injection Analysis
Cartridge Part Number 330356CT

Scope and Application

This method is used for determining the concentration of free cyanide in aqueous wastewater or effluent by flow injection analysis and amperometric detection according to **ASTM D7237-10**. This method is used in the USEPA's data gathering and monitoring programs associated with the Clean Water Act and NPDES permit compliance reporting. Free cyanide is defined as HCN, CN^-, and cyanide bound in metal-cyanide complexes that are easily dissociable into free CN^- ions at the pH of the aquatic environment ranging from pH 6 to pH 8.

Method Performance

Range	2.0–500 µg/L
Rate	30 samples/hour
Precision	1% RSD at mid-point of range
Method Detection Limit (MDL)	0.5 µg/L

The range may be extended to analyze other concentrations by changing the size of the sample loop.

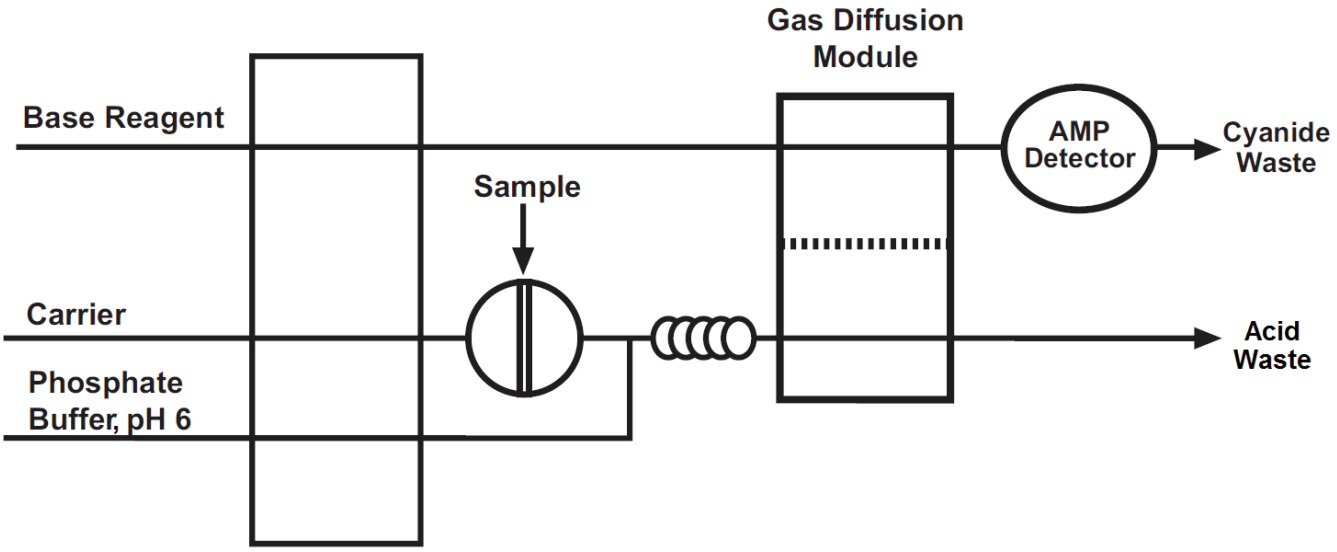


Figure 1. General flow diagram for Free Cyanide by ASTM D7237-10.

Reagents and Calibrants

Chemical Name	CAS #	Chemical Formula	Part Number
Cadmium potassium cyanide	14402-75-6	$K_2Cd(CN)_4$	
Potassium cyanide	151-50-8	KCN	
Sodium acetate	127-09-3	$C_2H_3O_2Na$	
Sodium hydroxide	1310-73-2	NaOH	A001103
Sodium phosphate, dibasic	7558-79-4	Na_2HPO_4	
Sodium phosphate, monobasic	7558-80-7	NaH_2PO_4	
Sulfuric acid, concentrated	7664-93-9	H_2SO_4	
Water, deionized		H_2O	
Zinc potassium cyanide	14244-62-3	$K_2Zn(CN)_4$	
Additionally, the following chemicals may be needed for sample preservation or treatment.			
Acetic acid, glacial	64-19-7	$C_2H_4O_2$	
Acetone	67-64-1	C_3H_6O	
Ascorbic acid	50-81-7	$C_6H_8O_6$	
5-[4-Dimethylaminobenzylidene]rhodanine	536-17-4	$C_{12}H_{12}N_2OS_2$	
Ethylenediamine	107-15-3	$C_2H_8N_2$	
Silver nitrate	7761-88-8	$AgNO_3$	
Sodium arsenite	7784-46-5	NaAsO	

Summary of ASTM D7237-10

Method

1. Aquatic free cyanide by gas diffusion amperometry (ASTM D7237-10) is based on the instrumentation and technology detailed in ASTM D6888, but employs milder conditions (a buffer with a pH range of 6 to 8 versus HCl or H_2SO_4), and does not use ligand displacement reagents.

2. A sample is injected into a carrier stream and mixed with a phosphate buffer at pH 6 to measure free cyanide (or pH 6 to pH 8 to measure aquatic free cyanide). Hydrogen cyanide gas (HCN) that is present diffuses across a hydrophobic membrane into an alkaline acceptor solution, where it converts back to ionic cyanide (CN^-). Cyanide is then carried into an amperometric flow cell where cyanide ions react with a silver working electrode, silver/silver chloride reference electrode, and platinum/stainless steel counter electrode at an applied potential of zero volts. The current generated is proportional to the cyanide concentration of the measured sample. The detector response is displayed as a peak. The resulting peak height is proportional to the cyanide concentration present in the sample.

Interferences

1. Method interferences can be caused by contaminants in the reagents, reagent water, and glassware, which may bias the results. Take care to keep all such items free of contaminants.

2. High levels of carbonate can release CO_2 into the acceptor stream and cause an interference with the amperometric detector, resulting in a slight masking effect (15% negative bias with 20 ppb cyanide in 1500 ppm carbonate).

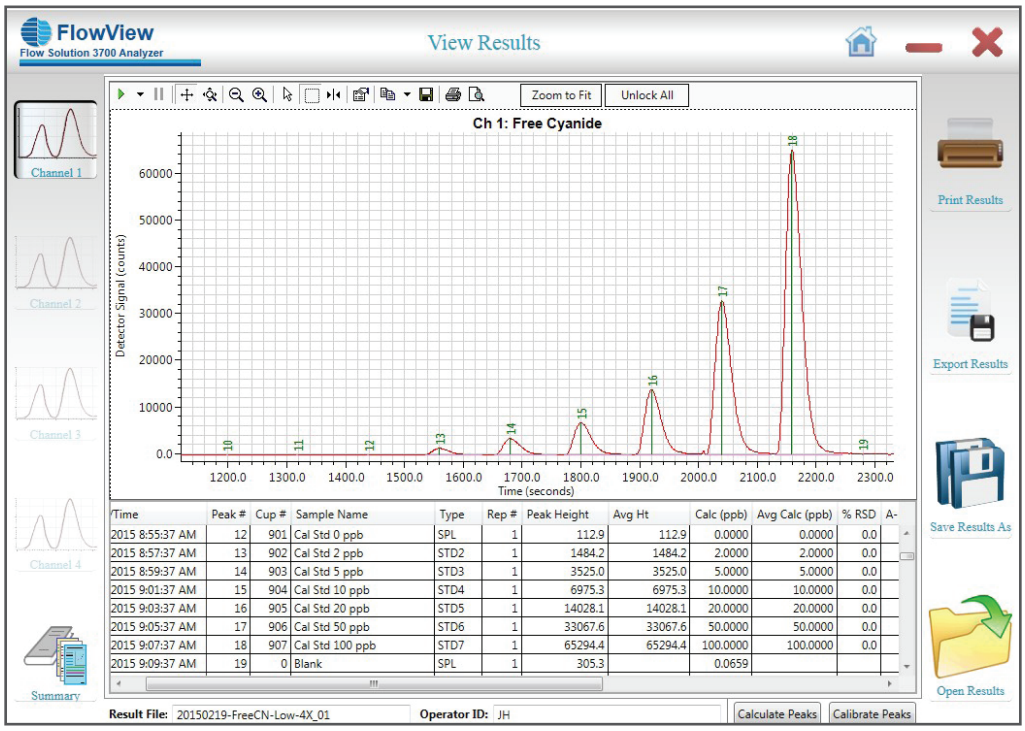
3. Sulfide above 50 mg/L will diffuse through the gas diffusion membrane and can be detected in the amperometric flowcell. Oxidized products of sulfide can also rapidly convert CN^- to SCN^- at high pH.

4. Oxidizing agents such as chlorine decompose most cyanides. Remove oxidizing agents that decompose cyanides by adding ascorbic acid if analysis is to be performed within 24 hours; otherwise, use sodium arsenite. Sample treatment is described in **Sample Handling and Preservation**.

5. Tests conducted on samples containing large amounts of colloids indicate rapid cyanide losses. Filter turbid or colloidal samples.

6. Nitrate and nitrite do not interfere in this method.

7. Thiocyanate, sulfite, and thiosulfate do not interfere with this method.



Time	Peak #	Cup #	Sample Name	Type	Rep #	Peak Height	Avg Ht	Calc (ppb)	Avg Calc (ppb)	% RSD
2015 8:55:37 AM	12	901	Cal Std 0 ppb	SPL	1	112.9	112.9	0.0000	0.0000	0.0
2015 8:57:37 AM	13	902	Cal Std 2 ppb	STD2	1	1484.2	1484.2	2.0000	2.0000	0.0
2015 8:59:37 AM	14	903	Cal Std 5 ppb	STD3	1	3525.0	3525.0	5.0000	5.0000	0.0
2015 9:01:37 AM	15	904	Cal Std 10 ppb	STD4	1	6975.3	6975.3	10.0000	10.0000	0.0
2015 9:03:37 AM	16	905	Cal Std 20 ppb	STD5	1	14028.1	14028.1	20.0000	20.0000	0.0
2015 9:05:37 AM	17	906	Cal Std 50 ppb	STD6	1	33067.6	33067.6	50.0000	50.0000	0.0
2015 9:07:37 AM	18	907	Cal Std 100 ppb	STD7	1	65294.4	65294.4	100.0000	100.0000	0.0
2015 9:09:37 AM	19	0	Blank	SPL	1	305.3		0.0659		

Figure 2. Free Cyanide Calibration Series

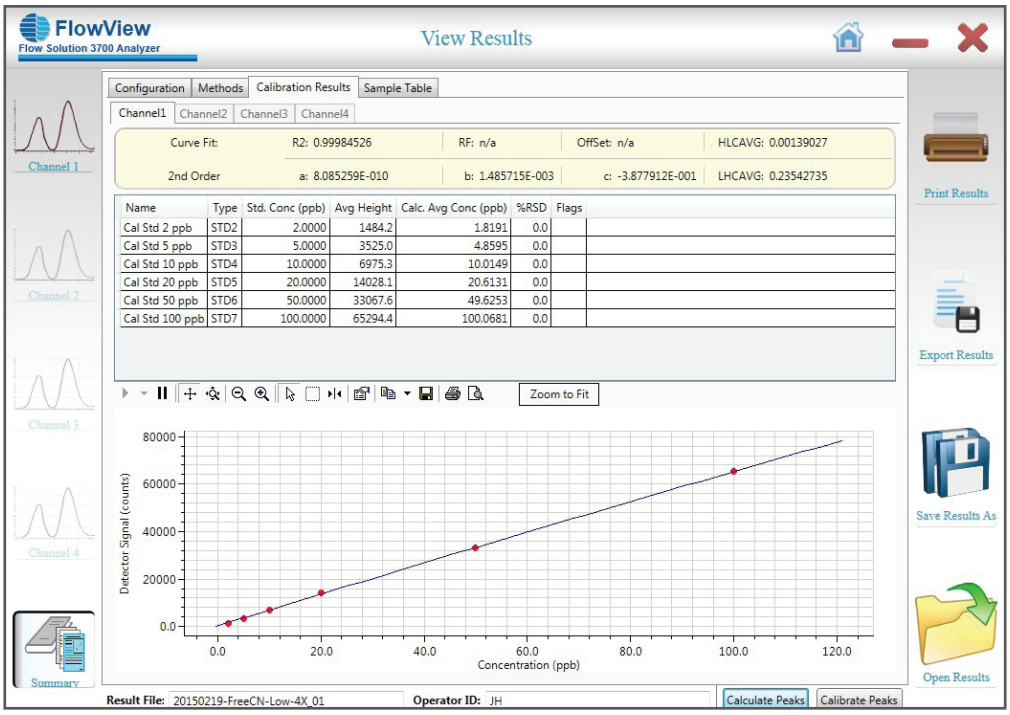


Figure 3. Calibration curve and statistics

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