

Flow Solution™ FS 3700 Automated Chemistry Analyzer

Total Cyanide by In-Line Ultraviolet Digestion and Amperometric Detection
ASTM D7511, Segmented Flow Injection Analysis
Cartridge Part Number 330090CT

Scope and Application

This method is used for determining total cyanide in drinking and surface waters, as well as domestic and industrial wastewaters by **ASTM method D7511**.^{1,2} Cyanide ion (CN⁻), hydrogen cyanide in water (HCN(aq)), and the cyano-complexes of zinc, copper, cadmium, mercury, nickel, silver, and iron may be determined by this method. Cyanide ions from Au(I), Co(III), Pd(II), and Ru(II) complexes are only partially determined.

Method Performance

Range	2.0–500 µg/L
Rate	30 samples/hour
Precision	<2% RSD at mid-point of range
Method Detection Limit (MDL)	1.0 µg/L

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

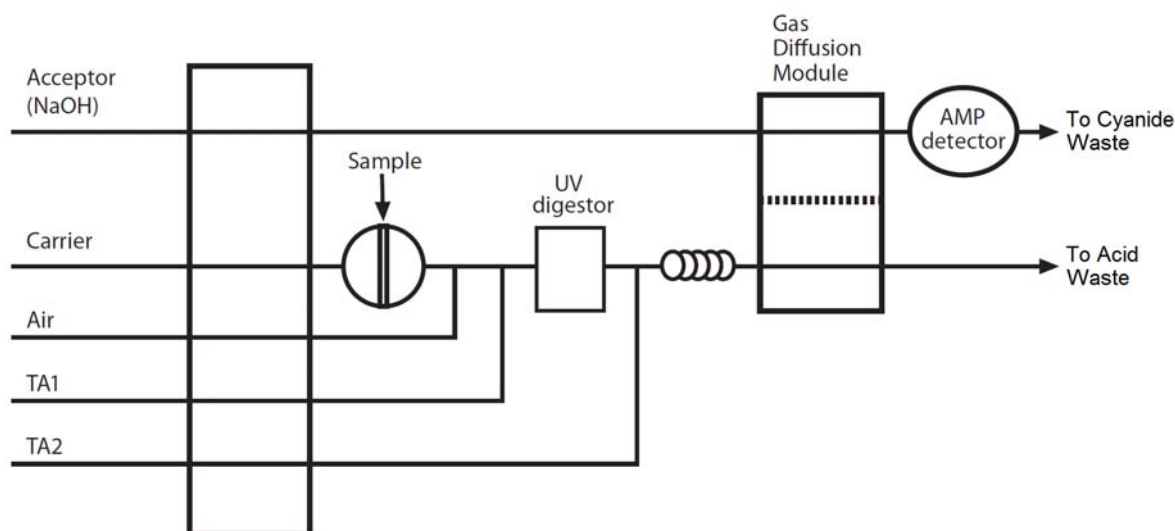


Figure 1. General Flow Diagram for Total Cyanide by ASTM D7511.

Reagents and Calibrants

Chemical Name	CAS #	Chemical Formula	Part Number
Ascorbic acid	50-81-7	$C_6H_8O_6$	
Bismuth nitrate pentahydrate	10035-06-0	$Bi(NO_3)_3 \cdot 5H_2O$	
Challenge Matrix, ASTM D7365			327788
Citric Acid	77-92-9	$C_6H_8O_7$	
OIA-1677/ASTM D7511 Control Standard			328942
Flow Solution - Total acid 1 (TA1)			A001505
Flow Solution - Total acid 2 (TA2)			A001872
Flow Solution - Total Carrier			A001688
Flow Solution - Base Reagent			A001103
Hypophosphorous acid	6303-21-5	H_3PO_2	
Potassium cyanide	151-50-8	KCN	
Potassium ferricyanide	13746-66-2	$K_3Fe(CN)_6$	
Potassium ferrocyanide	13943-58-3	$K_4Fe(CN)_6 \cdot 3H_2O$	
Sodium acetate	127-09-3	$C_2H_3O_2Na$	
Sodium hydroxide	1310-73-2	NaOH	
Sulfuric acid	7664-93-9	H_2SO_4	
Water, deionized		H_2O	
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	
5-(4-Dimethylaminobenzylidene)rhodanine	536-17-4	$C_{12}H_{12}N_2OS_2$	
Ethylenediamine	107-15-3	$C_2H_8N_2$	
Silver nitrate	7761-58-3	$AgNO_3$	
Sodium arsenite	7784-46-5	$NaAsO_2$	

Summary of ASTM D7511

Method

- Prior to analysis, treat the sample to remove potential interferences. Ultraviolet (UV) digestion releases cyanide from cyanide complexes. Acid addition converts cyanide ion to hydrogen cyanide gas (HCN), which passes under a gas diffusion membrane. The hydrogen cyanide gas diffuses through the membrane into an alkaline receiving solution, where it converts back to cyanide ion. A silver working electrode, silver/silver chloride reference electrode, and platinum/stainless steel counter electrode at an applied potential of zero volt amperometrically monitor the cyanide ion. The current generated is proportional to the cyanide concentration present in the original sample.

Interferences

- The practices in the most current ASTM D7365 “Standard Practices for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide” take precedence over sampling, preservation, and interference mitigation presented in this method.³
- Some of the known interferences to this method include aldehydes, carbonate, oxidizing agents, sulfide, surfactants, thiocyanate, and thiosulfate. Multiple interferences may require the analysis of a series of laboratory-fortified sample matrices (LFM) to verify the suitability of the chosen treatment. See below for details on some of these interferences and refer to **Sample Handling and Preservation** for treatments for mitigating various interferences.
- Samples that have been disinfected by UV irradiation are likely to contain aldehydes. Sample treatment is described in Sample Handling and Preservation for samples containing water soluble aldehydes, such as formaldehyde or acetaldehyde.
- High levels of carbonate can release CO₂ into the acceptor stream and cause an interference with the amperometric detector that results in a slight masking effect (15% negative bias with 20 ppb cyanide in 1500 ppm carbonate).^{1,2,3,4}
- Nitrate and nitrite do not interfere in this method; however, nitrite can react with organics in the sample to generate cyanide during storage. If nitrite concentration exceeding 2 ppm is expected, add sulfamic acid to sample at time of sampling.
- Oxidizing agents such as chlorine decompose most cyanides. Remove oxidizing agents that decompose cyanides. Sample treatment is described in **Sample Handling and Preservation**.
- Sulfide and sulfide-containing compounds may result in a positive interference in this method.^{5,6} When acidified, sulfide forms hydrogen sulfide, which passes through the gas diffusion membrane and produces a signal at the silver electrode. In addition, sulfide ions react with cyanide ions in solution to reduce its concentration over time. Treat samples containing sulfide according to **Sample Handling and Preservation**. During UV digestion, some sulfur compounds may produce sulfide. TA2 reagent contains a sulfide scrubber that removes up to 50 mg/L S²⁻ from the system prior to amperometric detection.
- High concentrations of surfactants interfere by changing the characteristics of the gas diffusion membrane, allowing acid solution to pass through the membrane and enter the detector.
- Thiocyanates can produce positive interference when they decompose to cyanide by UV radiation or oxidation.⁷ This method uses a narrowband 312 nm irradiation wavelength, which keeps interference from UV irradiation minimal. Use of modified Total Acid 1 reagent (TA1-M) minimizes interference from thiocyanate.

- Thiosulfate does not interfere at 20 ppm. Thiosulfate at 200 ppm may produce a slight positive bias. Sample treatment for high levels of thiosulfate is described in **Sample Handling and Preservation**.
- 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.

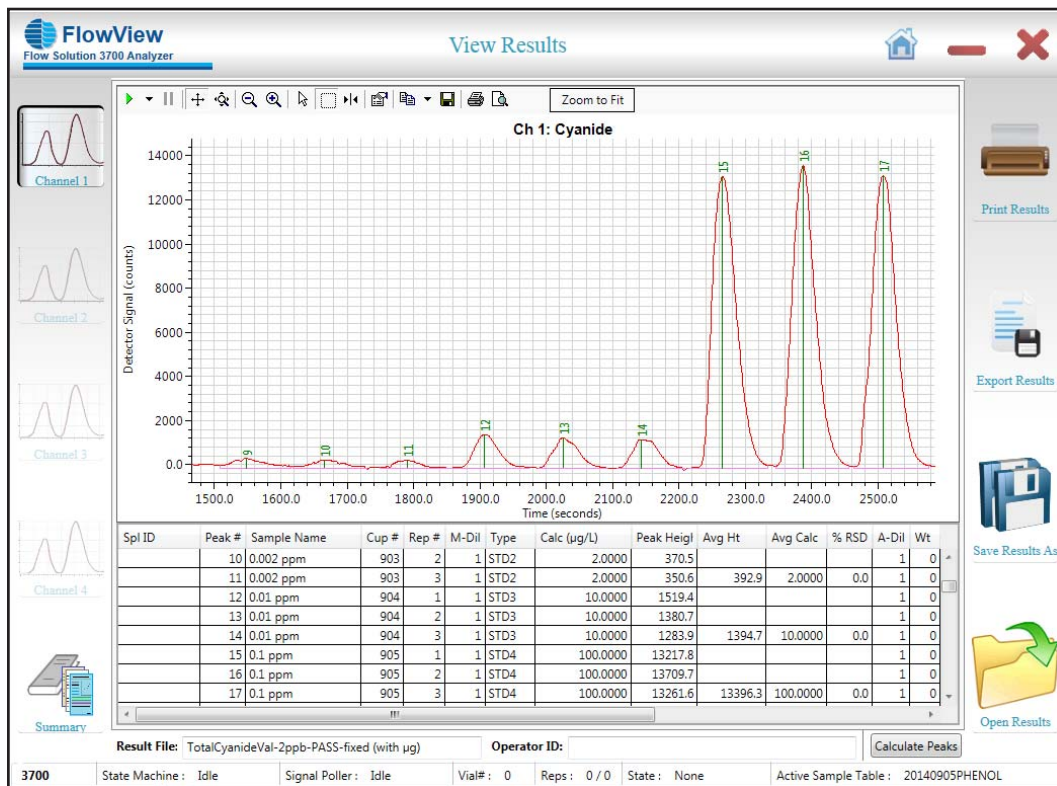


Figure 2. Total Cyanide Calibration Series

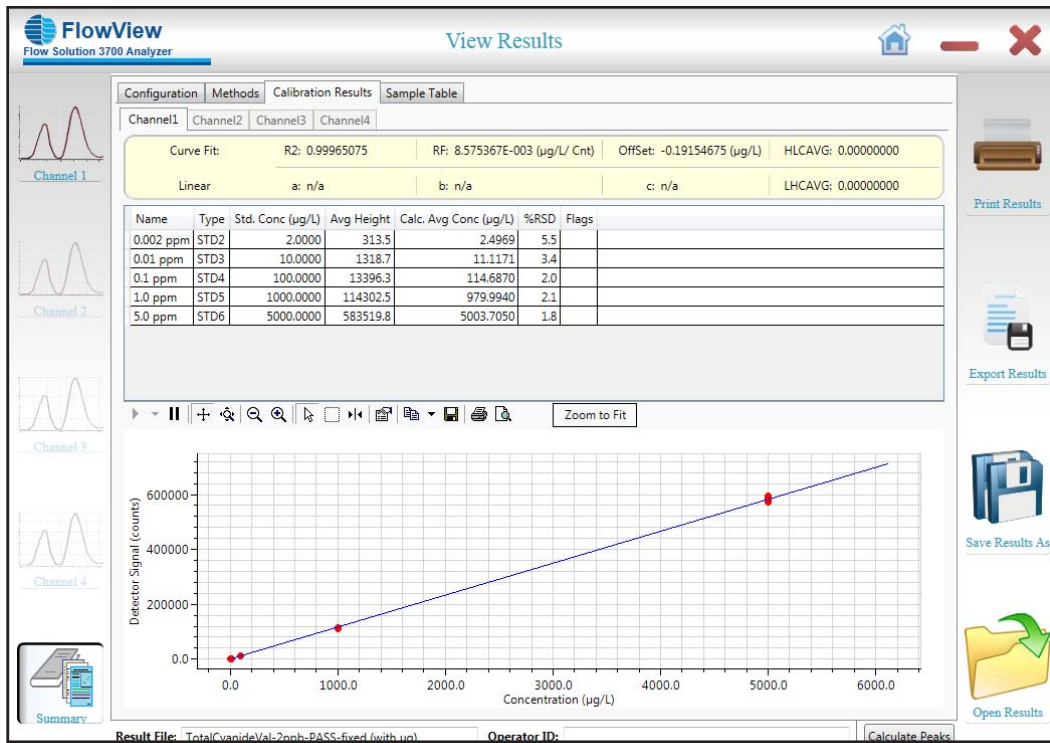


Figure 3. Calibration Curve and Statistics



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