

## Flow Solution™ FS 3700 Automated Chemistry Analyzer

Available Cyanide by Automated Ligand Exchange  
ASTM D6888, Flow Injection Analysis (FIA)  
Cartridge Part Number 330091CT

### Scope and Application

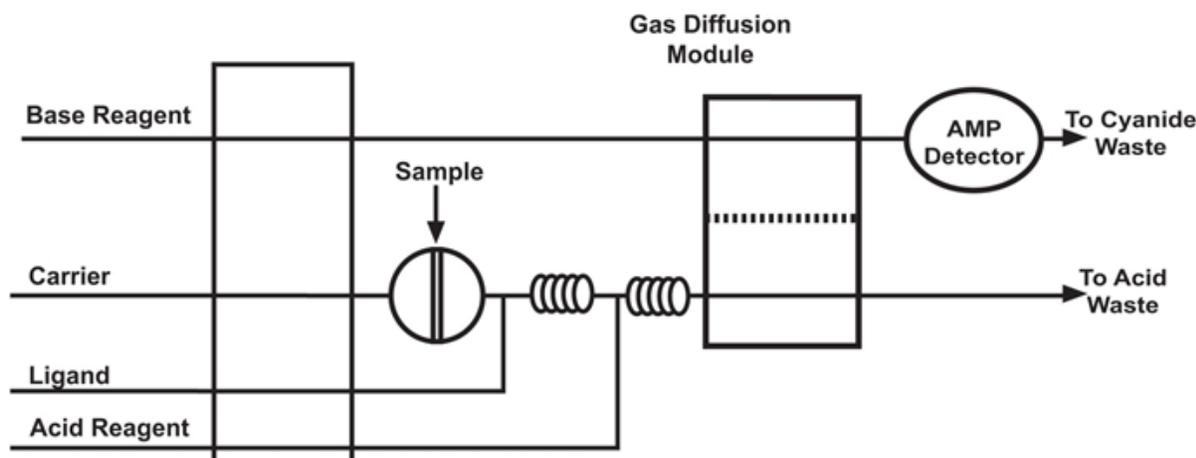
This method is used for determining available cyanide in water and wastewater by automated ligand exchange, flow injection analysis, and amperometric detection according to **ASTM Method D 6888-09**. This method is approved for use in the USEPA's data gathering and monitoring programs associated with the Clean Water Act.

Cyanide ion (CN<sup>-</sup>), hydrogen cyanide in water (HCN(aq)), and cyano-complexes of zinc, copper, cadmium, mercury, nickel, and silver can be determined by this method. The presence of polysulfides and colloidal material may prove intractable for application of this method.

### Method Performance

Range	5.0 µg/L–0.5 mg/L
Rate	30 samples/hour
Precision at 50 µg/L	<2% RSD
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. The quality of the analysis is assured through reproducible calibration and testing of the Flow Injection Analysis (FIA) system.



## Reagents and Calibrants

Chemical Name	CAS #	Chemical Formula	Part Number
Acetic acid, glacial	64-19-7	$C_2H_4O_2$	
Acetone	67-64-1	$C_3H_6O$	
Bismuth nitrate pentahydrate	10035-06-0	$Bi(NO_3)_3 \cdot 5H_2O$	
Water, deionized		$H_2O$	
5-[4-(Dimethylamino) benzylidene] rhodanine	536-17-4	$C_{12}H_{12}N_2OS_2$	
DOWFAX 2A1	12626-49-2		A000080
Ethylenediamine	107-15-3	$C_2H_8N_2$	
Ligand exchange reagent, available cyanide (WAD) reagent A			A001416
Ligand exchange reagent, available cyanide (WAD) reagent B			A001417
Mercury (II) cyanide	594-04-1	$Hg(CN)_2$	
Nickel potassium cyanide	14220-17-8	$K_2Ni(CN)_4$	
Potassium cyanide	151-50-8	KCN	
Silver nitrate	7761-58-3	$AgNO_3$	
Sodium acetate	127-09-3	$C_2H_3O_2Na$	
Sodium arsenite	7784-46-5	$NaAsO_2$	
Sodium hydroxide	1310-73-2	NaOH	
Sulfuric acid, concentrated	7664-93-9	$H_2SO_4$	
Sulfuric acidification reagent (SAR)			A001872

## Summary of ASTM D 6888

ASMT D 6888 summarizes the method and interferences as follows below.

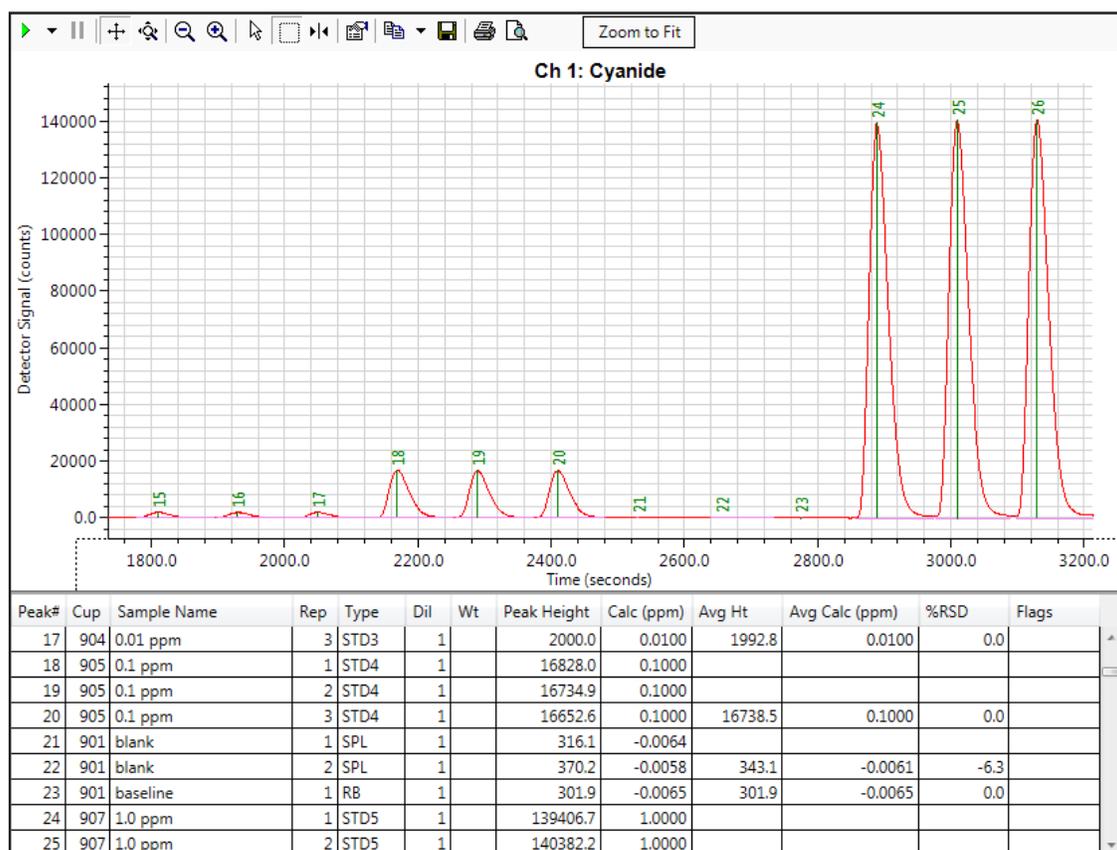
### Method

1. Before analysis, treat the sample to remove potential interferences. Ligand exchange reagents form thermodynamically stable complexes with the transition metal ions, releasing the cyanide ion from the cyano-complexes. Addition of acid converts the 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. The cyanide ion is monitored amperometrically with a silver working electrode, silver/silver chloride reference electrode, and platinum/stainless steel counter electrode at an applied potential of zero volt. The current generated is proportional to the cyanide concentration present in the original 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. Sulfide, at concentrations greater than 50 ppm, is a positive interferant in this method. When sulfide is acidified, it forms hydrogen sulfide, which passes through the gas diffusion membrane and produces a signal at the silver electrode. In addition, sulfide ion reacts with cyanide ion in solution to reduce its concentration over time.
3. Treat samples containing water soluble aldehydes, such as formaldehyde or acetaldehyde, by adding ethylenediamine solution, at the time of sampling.

4. Remove oxidizing agents that decompose cyanides by adding ascorbic acid if analysis is to be within 24 hours, otherwise use sodium arsenite.
5. High concentrations of carbonate can result in a negative response in the amperometric detector when carbon dioxide diffuses across the gas diffusion membrane into the alkaline receiving solution, reducing its pH. Treat effluents from high-carbonate containing wastes, such as coal gasification waste and atmospheric emission scrub water, with hydrated lime to stabilize the sample (Reference 11).
6. Tests conducted on samples containing large amounts of colloids indicate rapid cyanide losses. Filter turbid or colloidal samples.
7. Nitrate and nitrite do not interfere in this method.
8. Thiocyanate, sulfite, and thiosulfate do not interfere with this method.



**Figure 2.** Available Cyanide Calibration Series

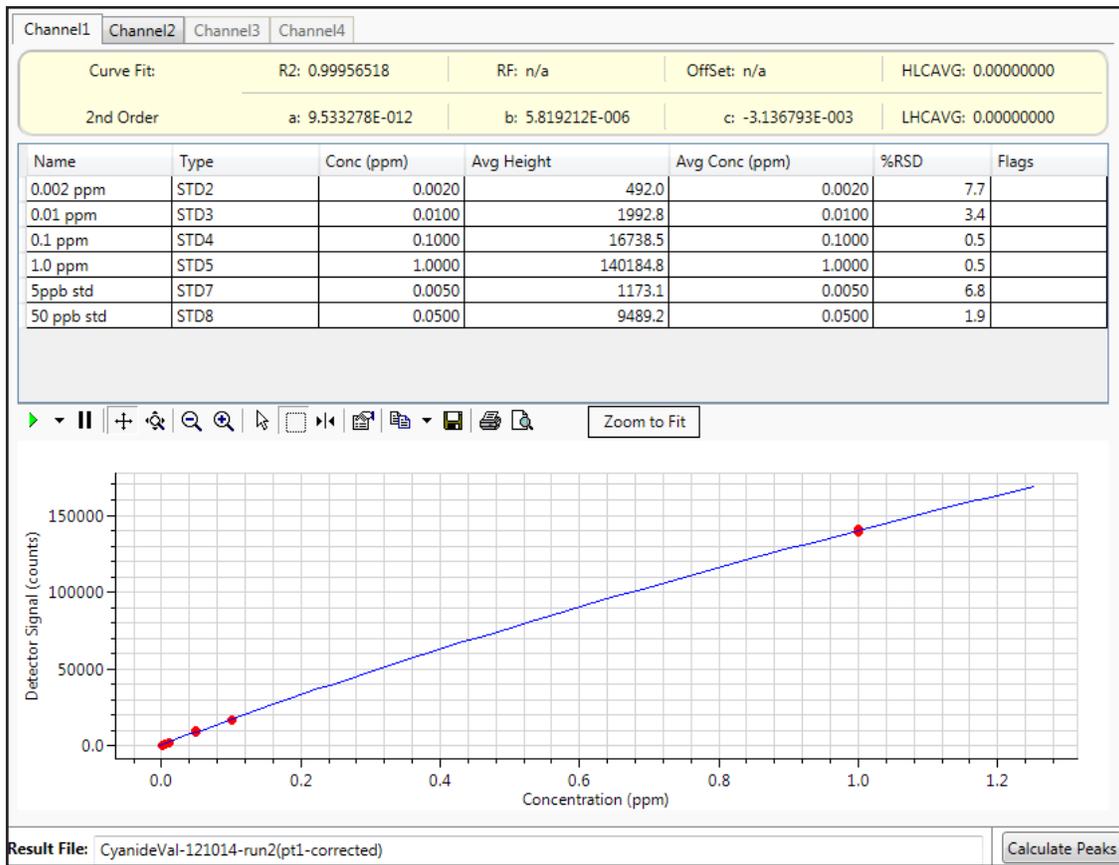


Figure 3. Calibration Curve and Statistics



151 Graham Road  
 PO Box 9010  
 College Station, Texas  
 77842-9010  
 (979) 690-1711  
 (800) 653-1711 USA/Canada  
 (979) 690-0440 Fax  
 www.oico.com  
 E-mail: OI-Mail@Xyleminc.com