

Method Abstract

Summary:

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 (HCN) gas, which passes under a gas diffusion membrane. HCN 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:

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

Treat samples containing sulfide, which is a positive interferent in this method. When acidified, sulfide 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. During UV digestion, some sulfur compounds may produce sulfide. TA 2 reagent contains a sulfide scrubber that can remove up to 50 mg/L S²⁻ from the system prior to amperometric detection.

Treat sample containing water soluble aldehydes, such as formaldehyde or acetaldehyde, by adding ethylenediamine solution.

Remove oxidizing agents that decompose cyanides by adding ascorbic acid.

Thiocyanates can produce positive interferences when they decompose to cyanide by UV radiation. This method uses 312 nm as the irradiation wavelength, which keeps thiocyanate interference minimal.

High carbonate concentrations 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.

High surfactant concentrations interfere by changing the characteristics of the gas diffusion membrane, allowing acid solution to pass through the membrane and enter the detector.

Nitrate and nitrite do not interfere in this method.

Performance Specifications:

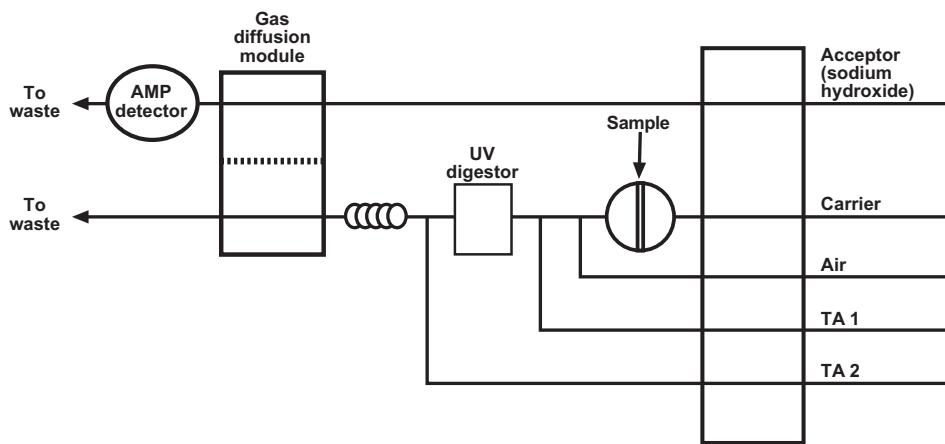
Range	2.0 µg/L–5.0 mg/L
Throughput	30 samples/hour
Precision at 50 µg/L	<3% RSD
500 µg/L	<2% RSD
Method Detection Limit (MDL)	0.5 µg/L



Parameter	Required Recovery Range (%)	Precision
Matrix spike/matrix spike duplicate	70–130	<11% RSD
Laboratory control standard, 2.00 mg/L	>70	5% RSD
Laboratory control standard, 0.200 mg/L	73–127	5% RSD

Chemicals:

Acetic acid, glacial, C ₂ H ₄ O ₂	Potassium ferricyanide, K ₃ Fe(CN) ₆ or potassium ferrocyanide, K ₄ Fe(CN) ₆ •3H ₂ O
Acetone, C ₃ H ₆ O	Silver nitrate, AgNO ₃
Brij®-35, 30% w/v (PN A21-0110-33)	Sodium acetate, anhydrous, C ₂ H ₃ O ₂ Na
Carrier solution (PN A001668)	Sodium hydroxide, NaOH
5-[4-(Dimethylamino)benzylidene]rhodanine, C ₁₂ H ₁₂ N ₂ OS ₂	Sulfuric acid, concentrated, H ₂ SO ₄
Ethylenediamine, anhydrous, C ₂ H ₈ N ₂	Total acid 1 (TA 1) reagent (PN A001505)
Potassium cyanide, KCN	Total acid 2 (TA 2) reagent (PN A001872)

Basic Flow Diagram:

Selected References:

Ingersol, D.; Harris, W.R.; Bomberger, D.C.; Coulson, D.M. *Development and Evaluation Procedures for the Analysis of Simple Cyanides, Total Cyanides, and Thiocyanate in Water and Waste Water: 1983*; EPA-600/4-83-054; U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, U.S. Government Printing Office: Washington, DC, 1983.

Standard Test Methods for Cyanides in Water. *Annual Book of ASTM Standards Volume 11.02*, ASTM International; ASTM D6888-04.

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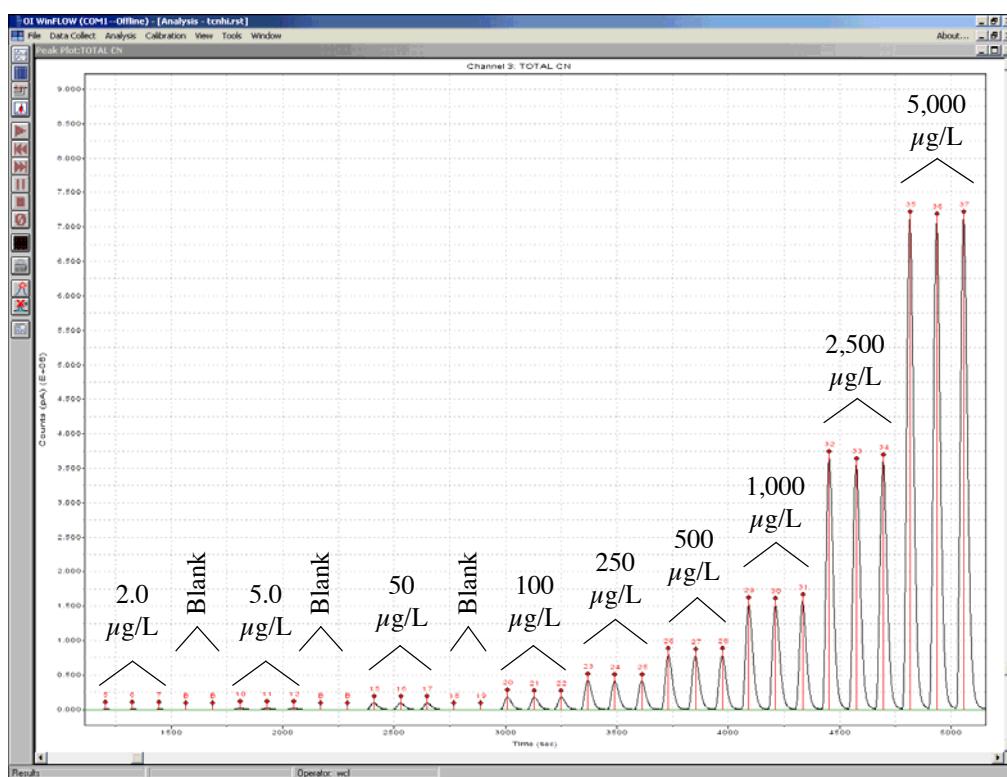
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Figures


Figure 1. Total cyanide calibration (2.0–5,000 µg/L)

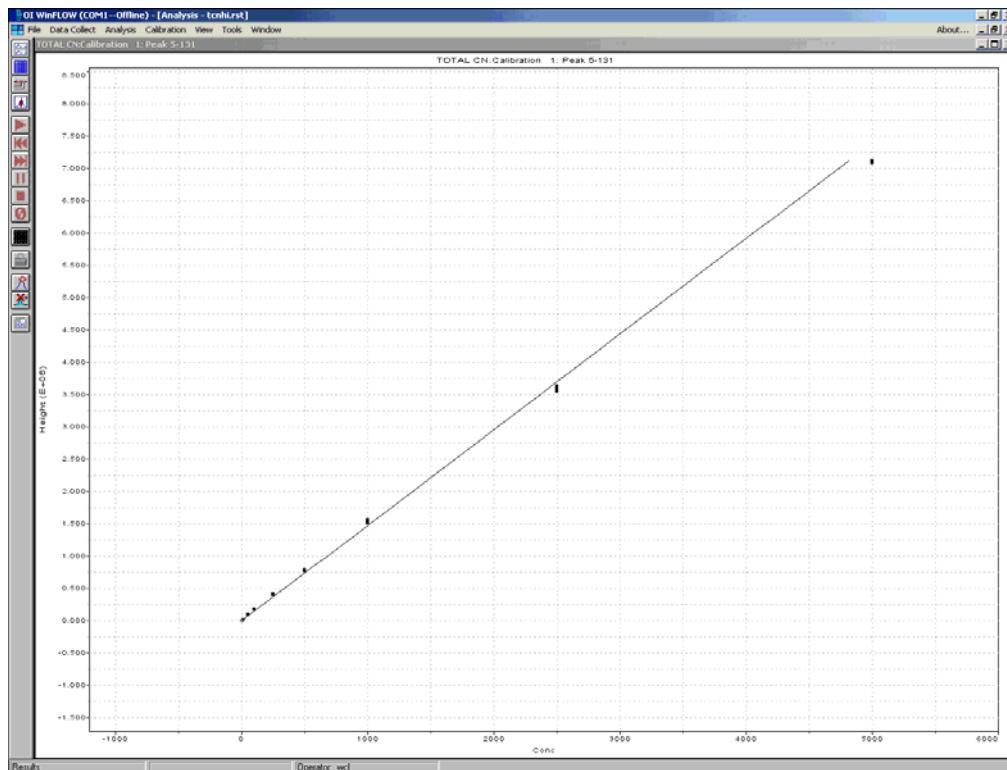


Figure 2. Total cyanide calibration curve (2.0–5,000 µg/L)

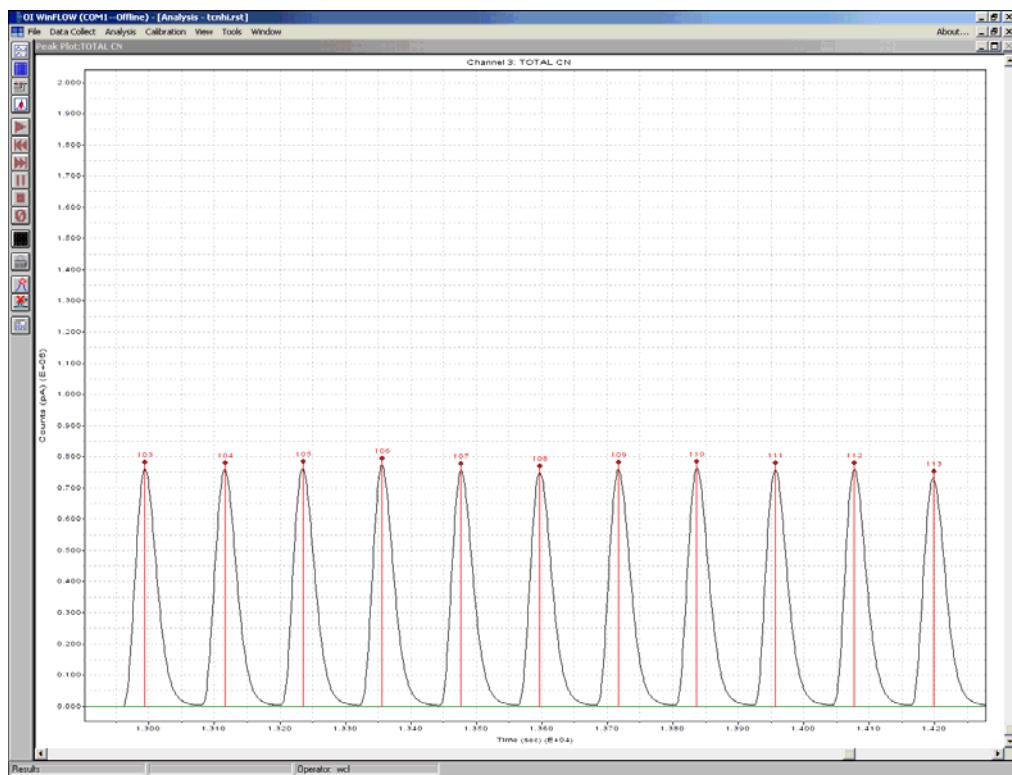
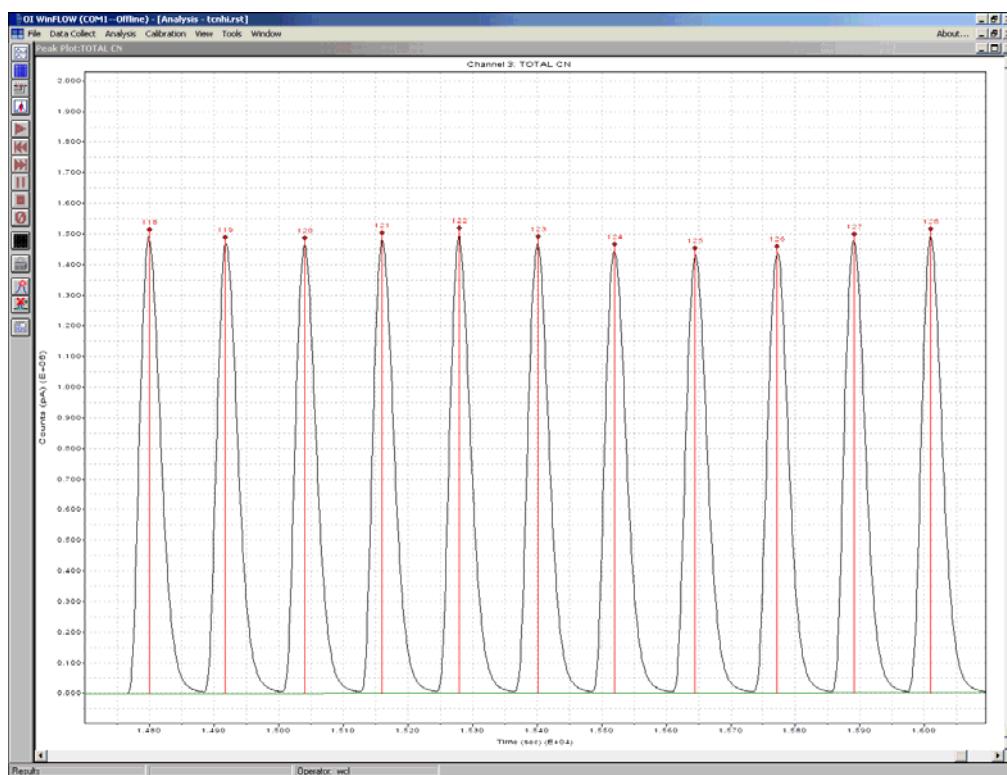
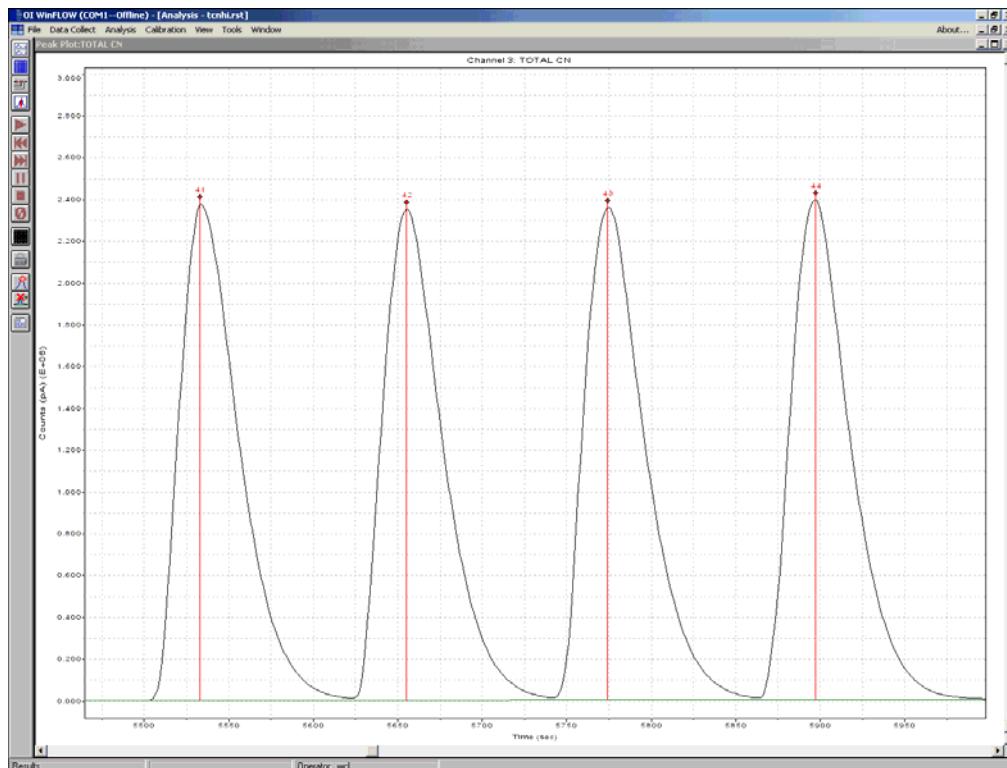


Figure 3. Total cyanide precision at 500 µg/L (<3% RSD)

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 Figure 4. Total cyanide precision at 1,000 $\mu\text{g/L}$ (<2% RSD)

 Figure 5. LCS precision at 2,000 $\mu\text{g/L}$ (<1% RSD)

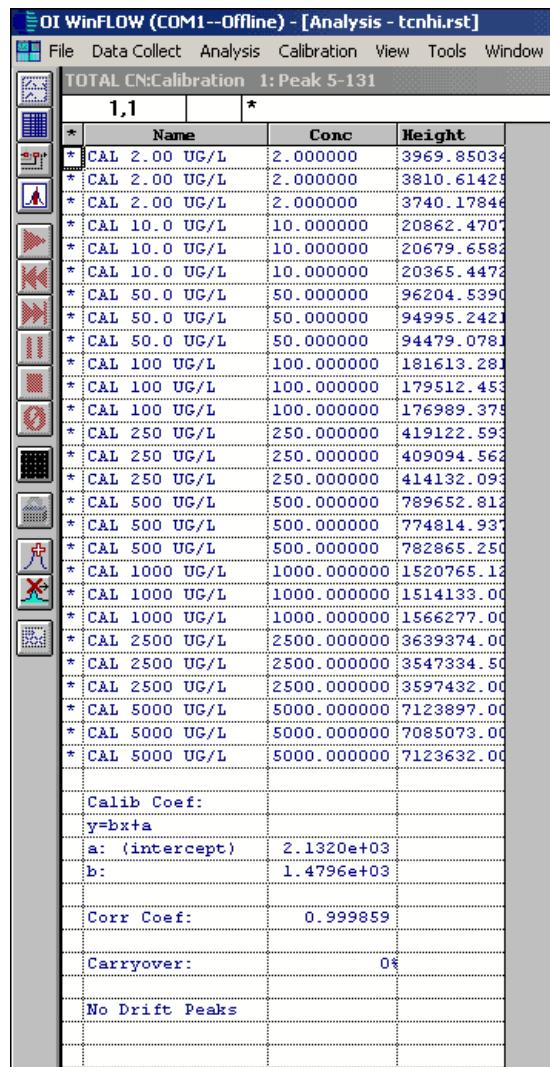
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Figure 6. Total cyanide calibration results (2.0–5,000 µg/L)

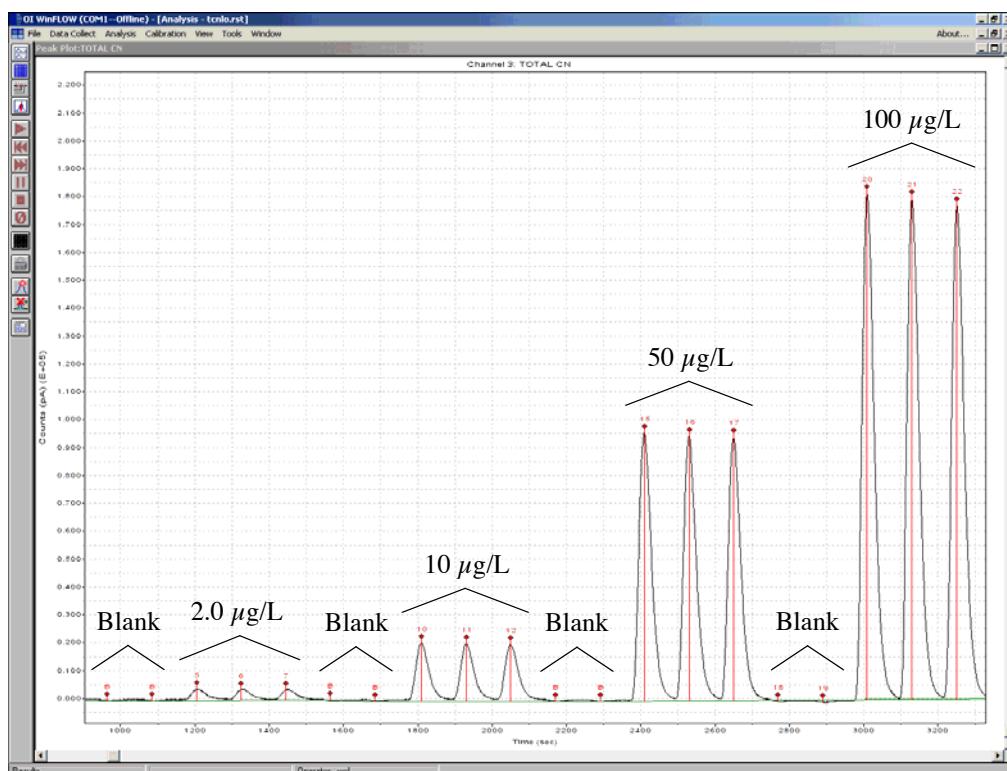
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Figure 7. Total cyanide calibration (2.0–100 µg/L)

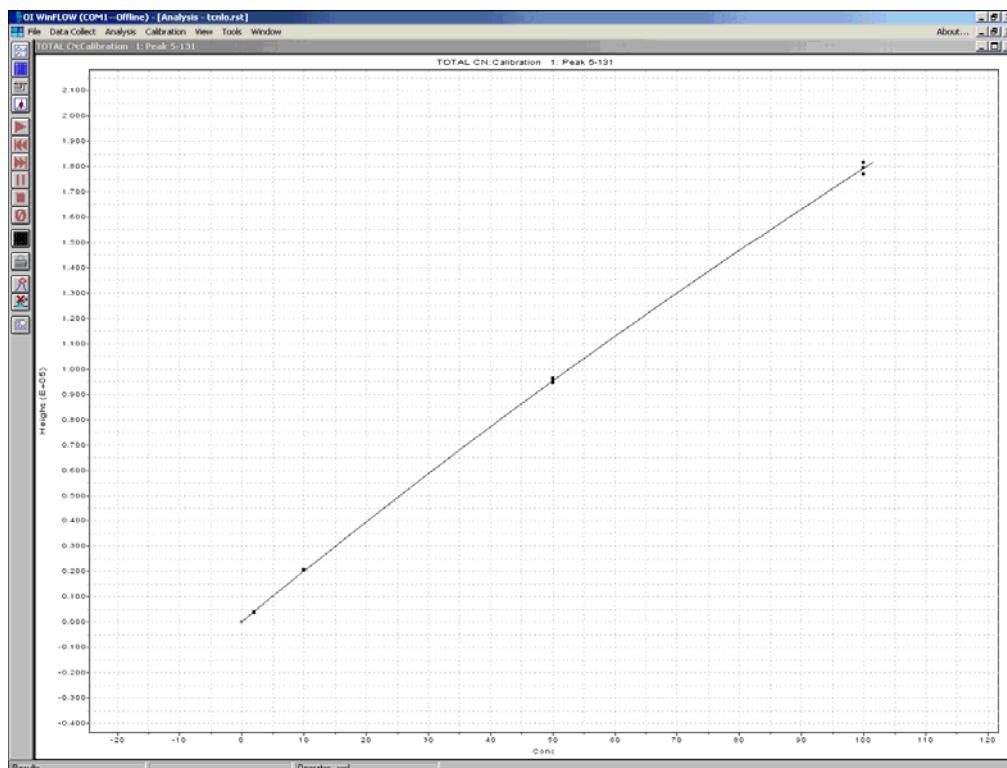
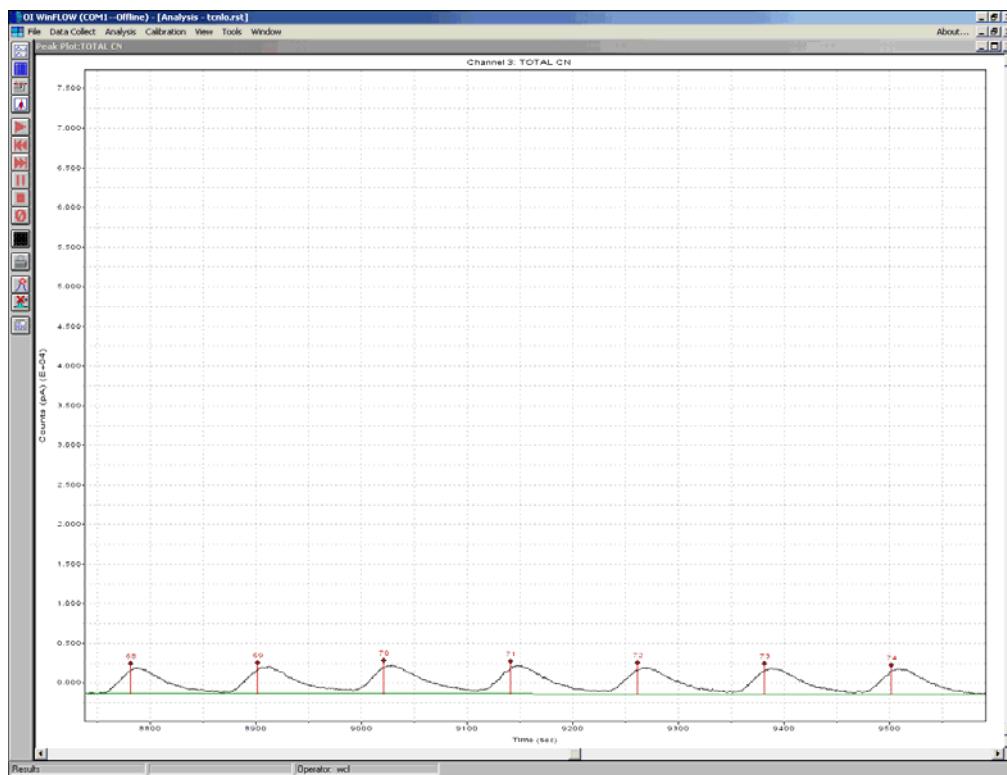
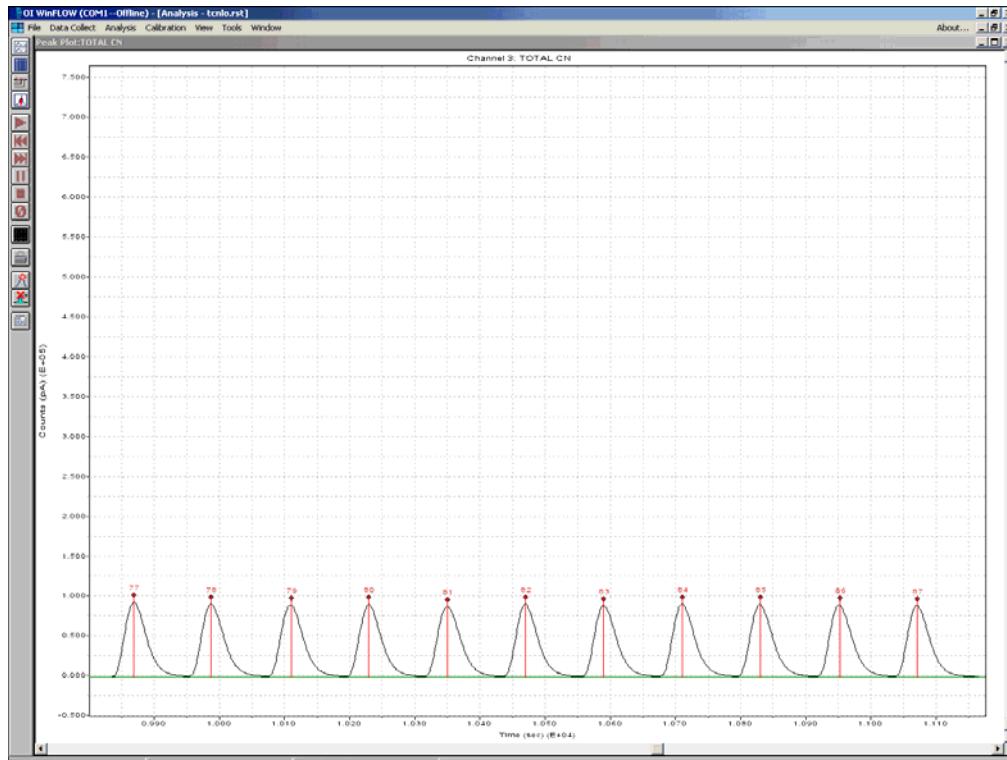


Figure 8. Total cyanide calibration curve (2.0–100 µg/L)

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 Figure 9. Total cyanide precision at $2.0 \mu\text{g/L}$

 Figure 10. Total cyanide precision at $50 \mu\text{g/L}$

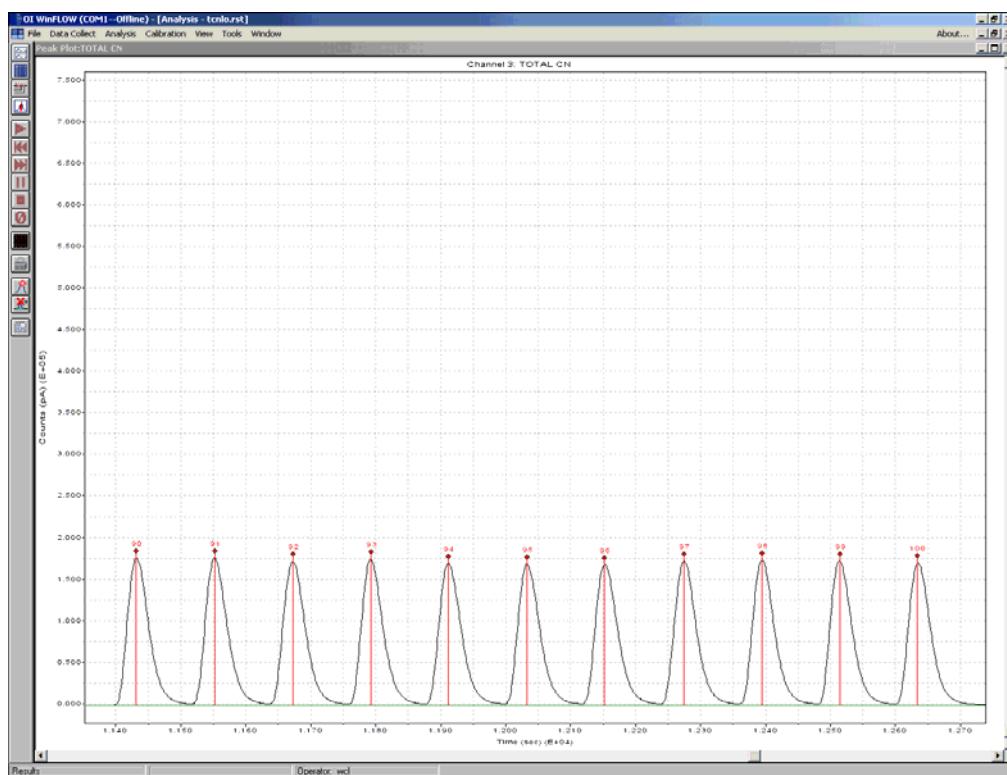
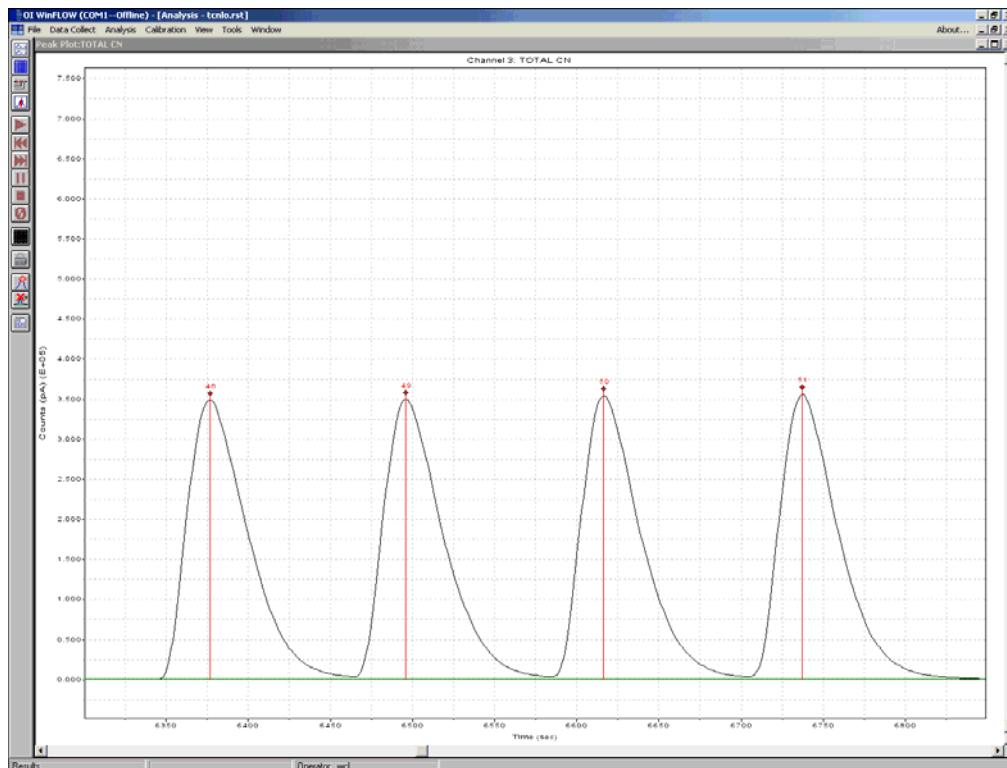
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 Figure 11. Total cyanide precision at 100 $\mu\text{g/L}$


Figure 12. Quality control standard

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(Synthetic wastewater, in-house preparation, 244 µg/L CN as an Fe(III) complex)

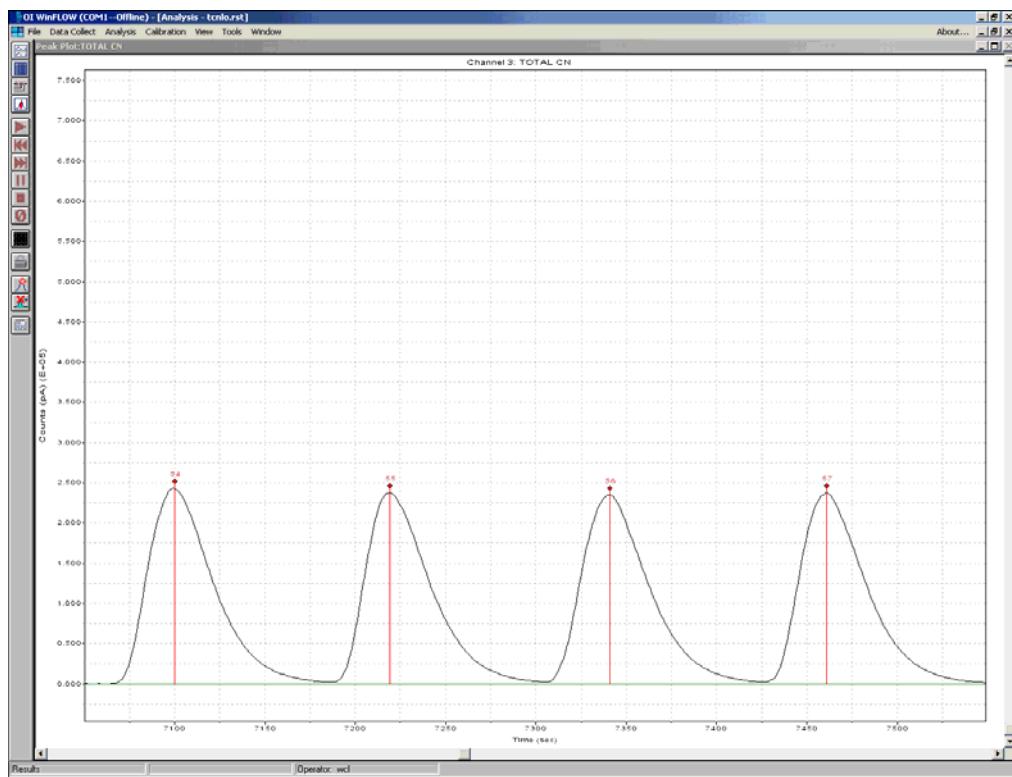


Figure 13. Quality control standard
 (WasteWatR™ cyanide and phenol, catalog number 502,
 Environmental Resource Associates)

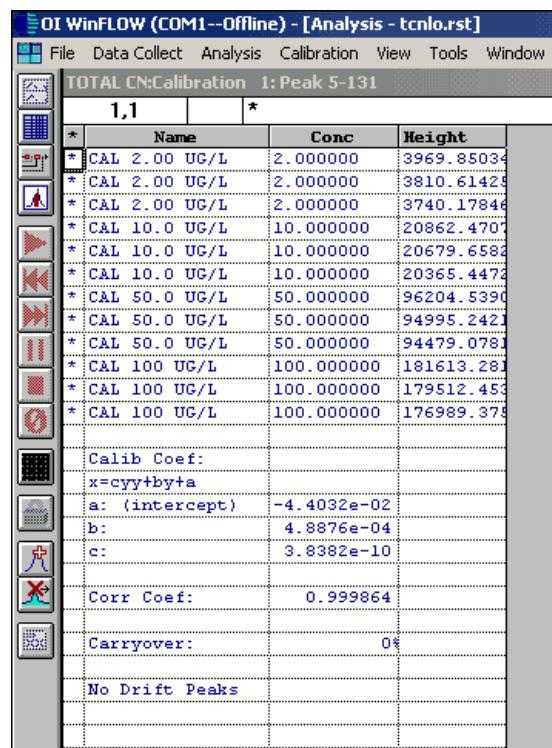
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Figure 14. Total cyanide calibration results (2.0–100 µg/L)