

Method Abstract

Summary:

Prior to analysis, treat the sample to remove potential interferences. Add ligand exchange reagents to the sample. Thermodynamically stable complexes form with the transition metal ions, releasing cyanide ion from cyano-complexes. Inject an aliquot of the treated sample into the FIA system. Adding hydrochloric acid 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 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.

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.

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.

Tests conducted on samples containing large amounts of colloids indicate rapid cyanide losses. Filtration can be used to remove colloids, but measured cyanide levels may be adversely affected.

Nitrate and nitrite do not interfere in this method.

Performance Specifications:

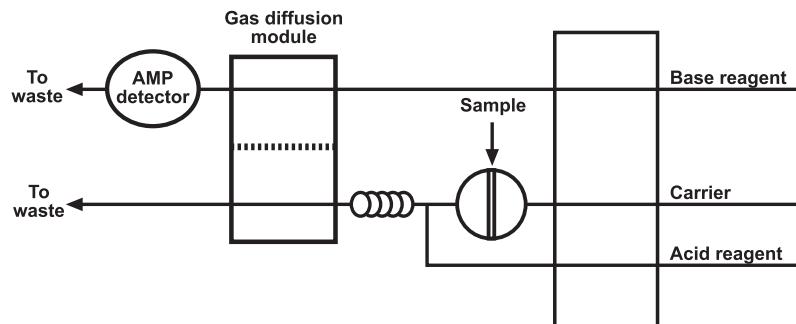
Range	2.0 µg/L–5.0 mg/L
Throughput	30 samples/hour
Precision at	<3% RSD
2.0 µg/L	<2% RSD
50 µg/L	<1% RSD
500 µg/L	<1% RSD
5.0 mg/L	<1% RSD
Method Detection Limit (MDL)	0.5 µg/L

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Parameter	Required Recovery Range (%)	Precision
Initial precision and recovery	92–122	<5.1% RSD
Ongoing precision and recovery	82–132	n/a
Matrix spike/matrix spike duplicate	82–130	<11% RSD
Calibration verification	86–118	n/a

Chemicals:

Acetic acid, glacial, C ₂ H ₄ O ₂	Mercury(II) cyanide, Hg(CN) ₂
Acetone, C ₃ H ₆ O	Nickel(II) cyanide, Ni(CN) ₂
Available cyanide reagent A (PN A001416)	Potassium cyanide, KCN
Available cyanide reagent B (PN A001417)	Silver nitrate, AgNO ₃
Bismuth nitrate pentahydrate, (Bi(NO ₃) ₃ •5H ₂ O	Sodium acetate, anhydrous, C ₂ H ₃ O ₂ Na
5-[4-(Dimethylamino)benzylidene]rhodanine, C ₁₂ H ₁₂ N ₂ OS ₂	Sodium hydroxide, NaOH
Ethylenediamine, anhydrous, C ₂ H ₈ N ₂	Sulfuric acid, concentrated, H ₂ SO ₄

Basic Flow Diagram:

Note:

This method complies with USEPA Method OIA-1677 and ASTM Method D6888-04.

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.



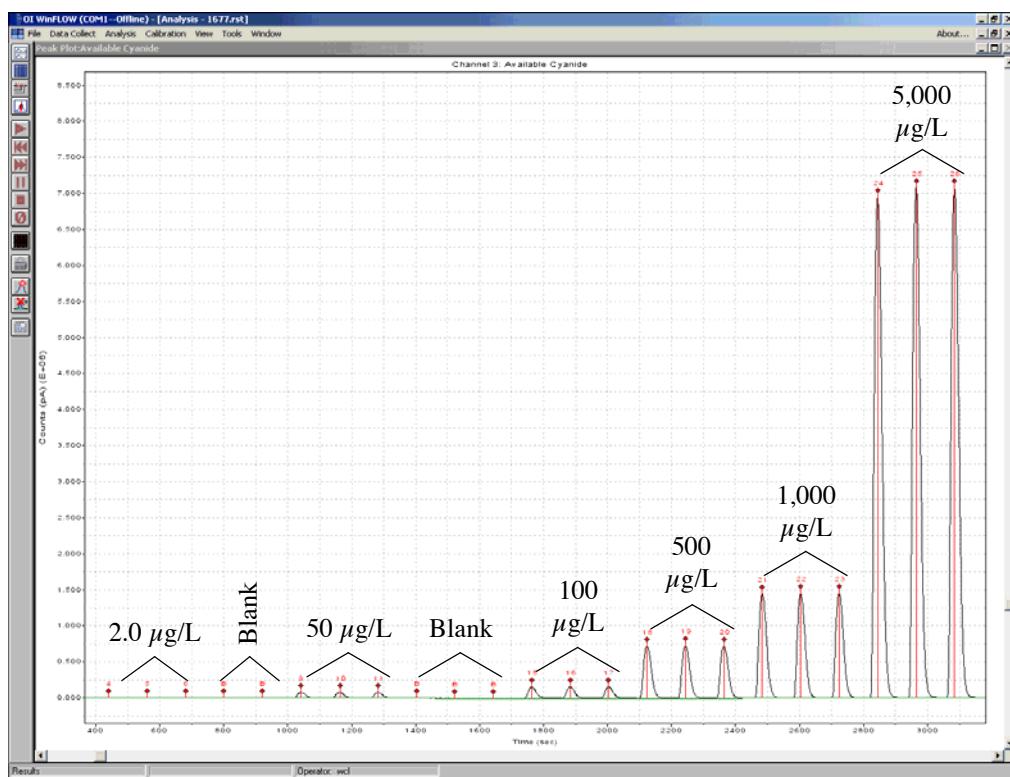
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Figures


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

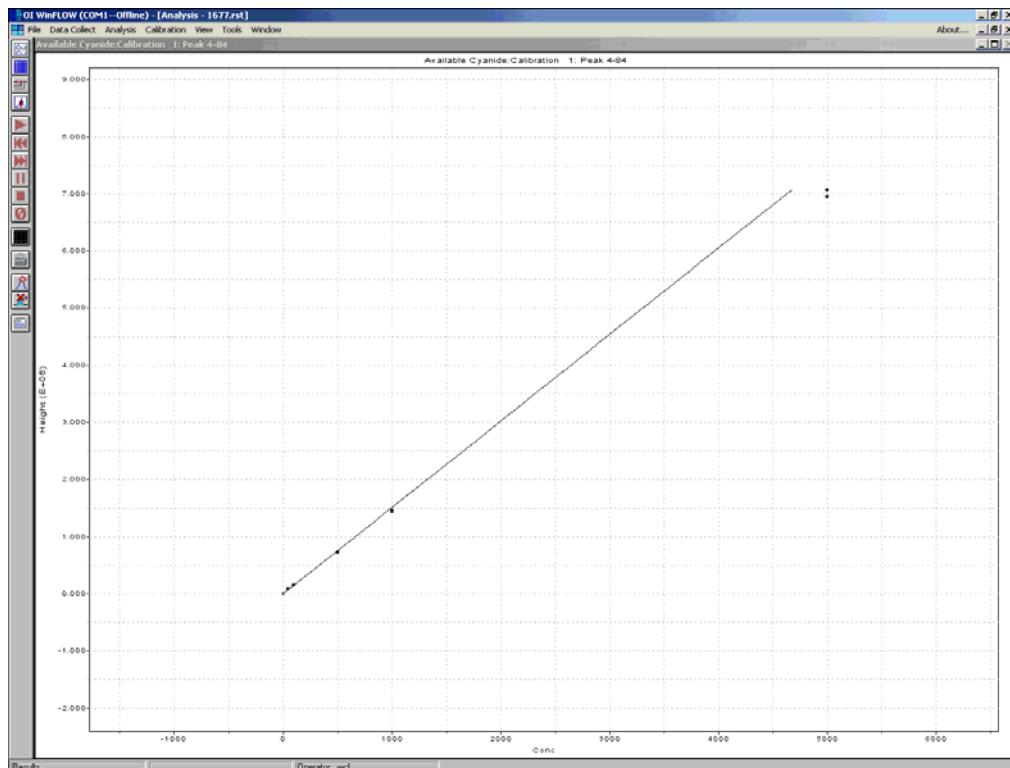


Figure 2. Available cyanide calibration curve (2.0–5,000 µg/L)

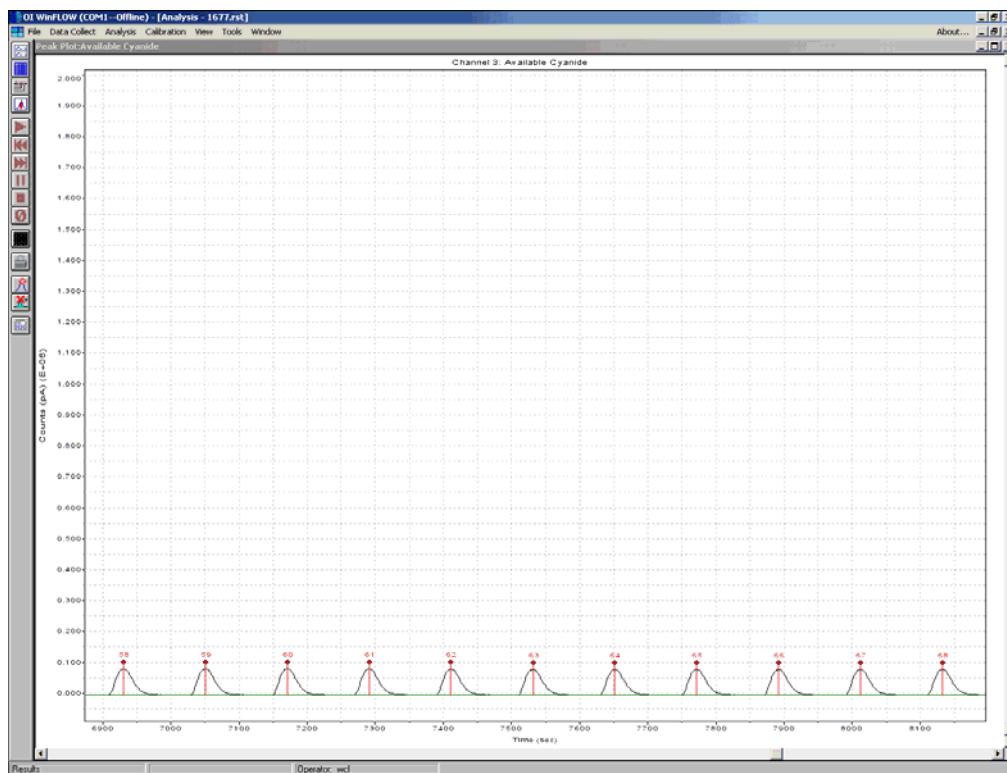
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Figure 3. Available cyanide precision at 50 µg/L (<2% RSD)

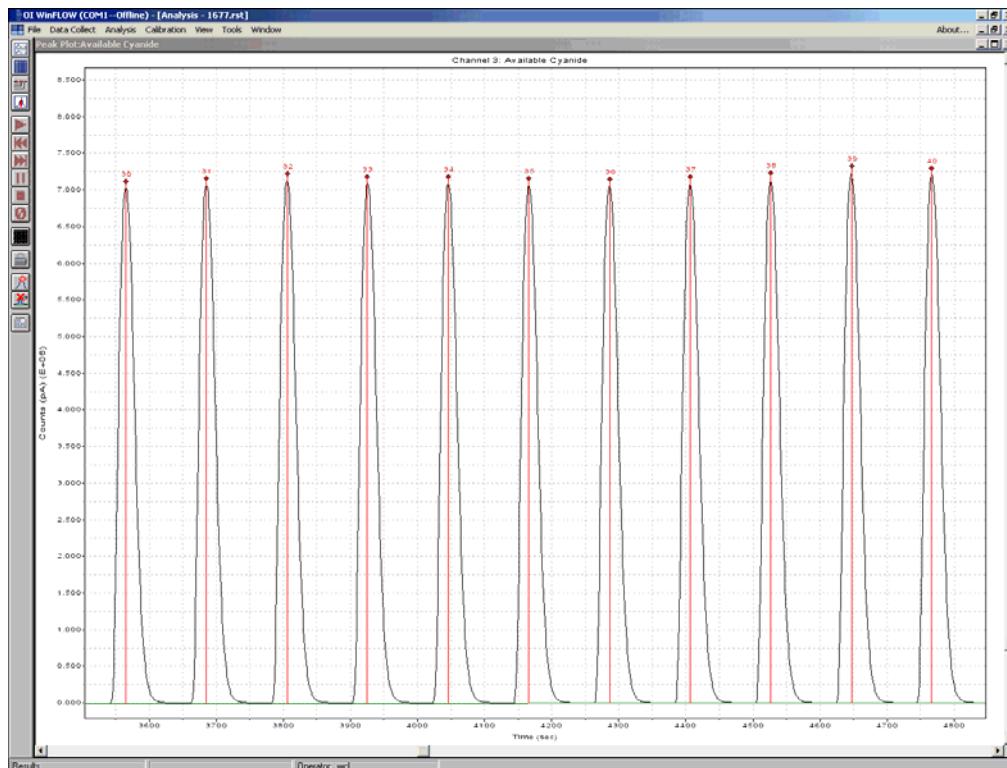


Figure 4. Available cyanide precision at 5,000 µg/L (<2% RSD)

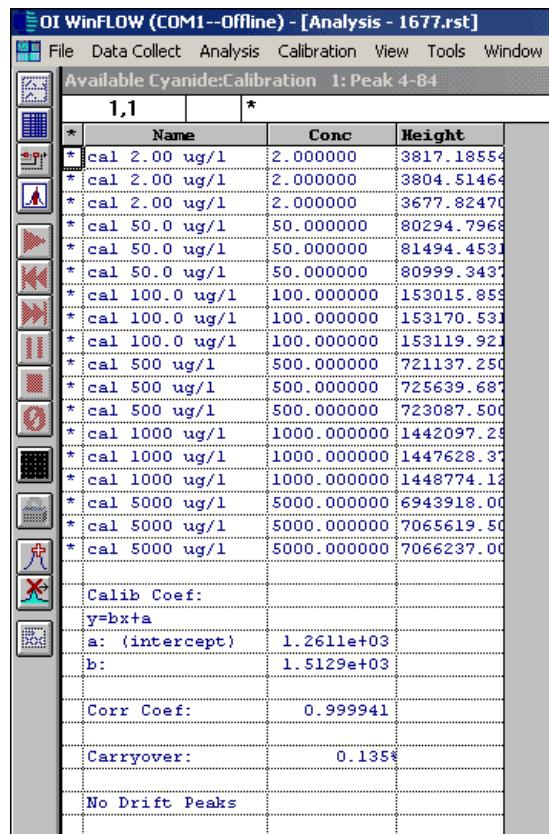
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Figure 5. Available cyanide calibration results (2.0–5,000 µg/L)

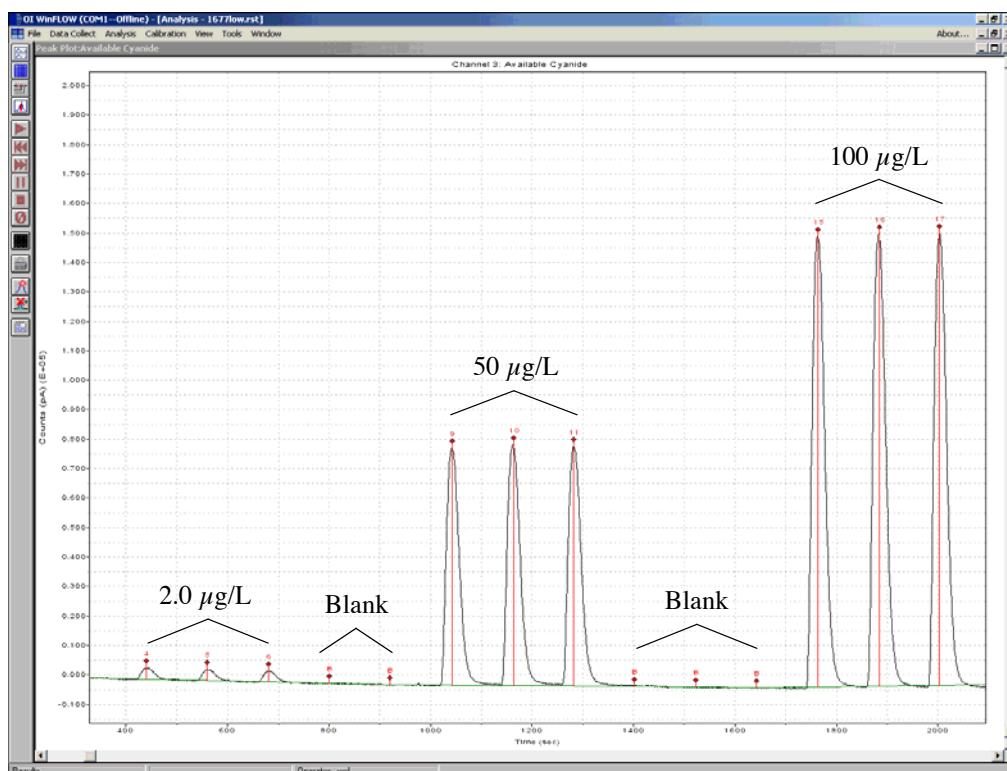
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Figure 6. Available cyanide calibration (2.0–100 µg/L)

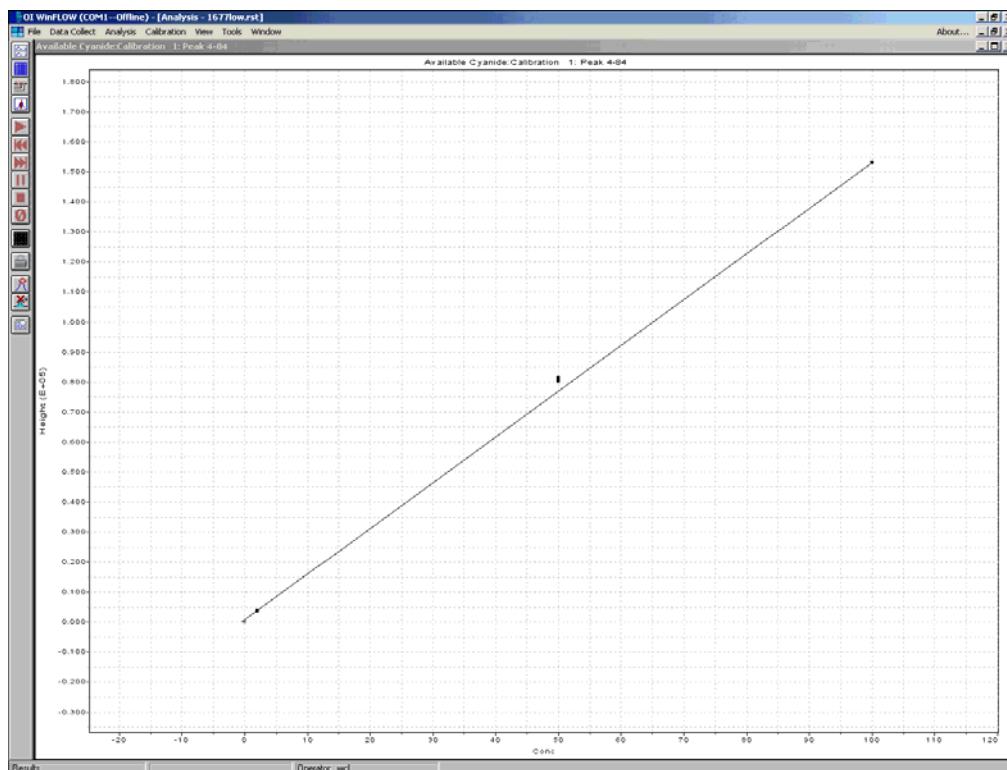
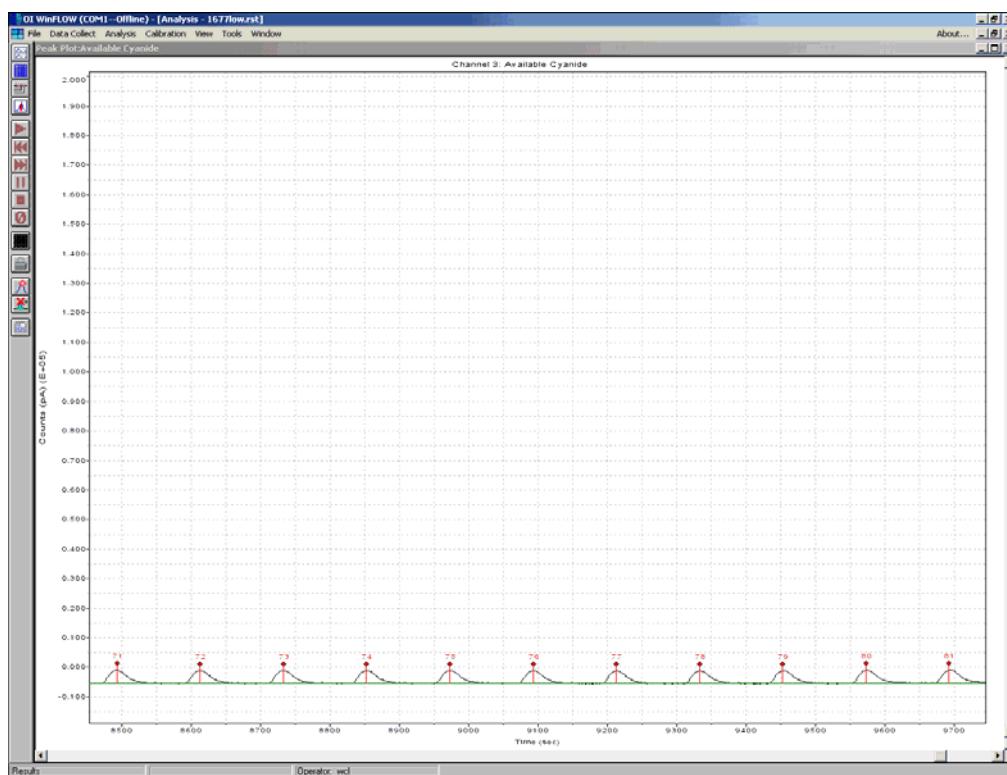
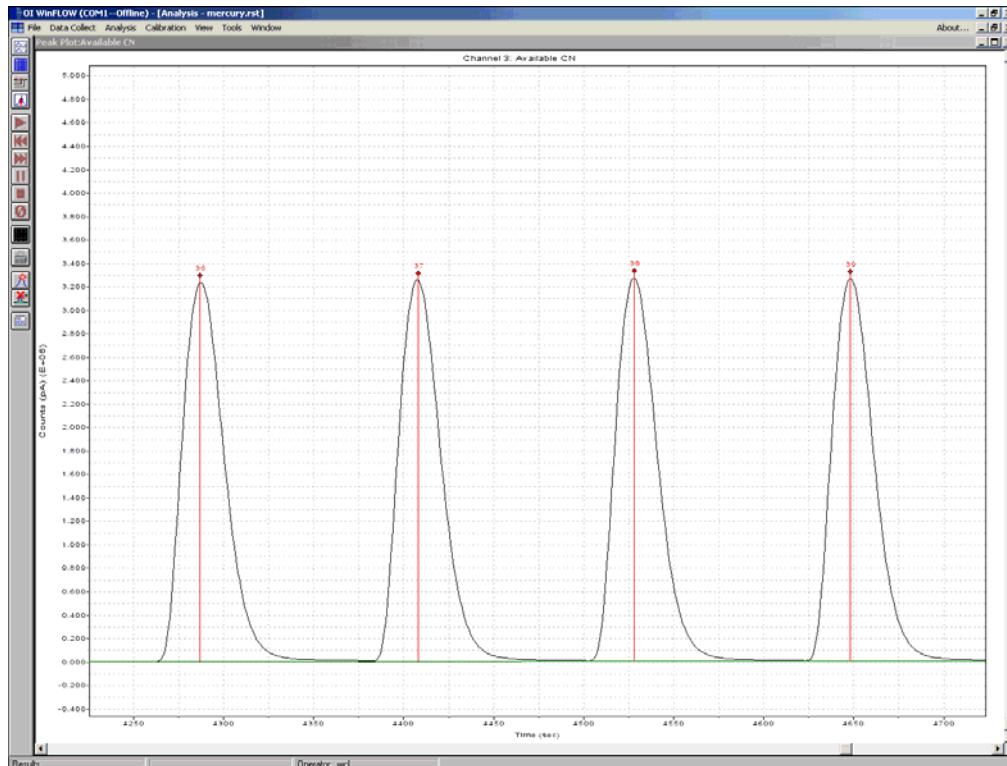


Figure 7. Available cyanide calibration curve (2.0–100 µg/L)

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 Figure 8. Available cyanide precision at 2.0 $\mu\text{g/L}$ (<4% RSD)

 Figure 9. LCS precision at 2,000 $\mu\text{g/L}$ (<1% RSD)

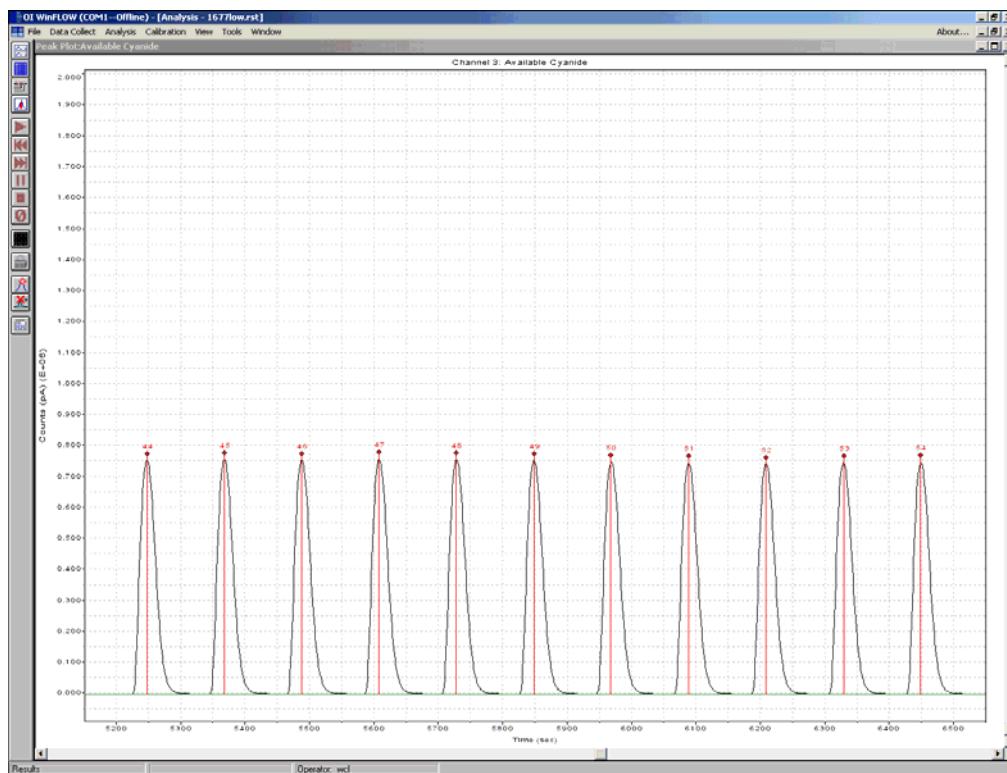
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Figure 10. Available cyanide precision at 500 µg/L (<2% RSD)

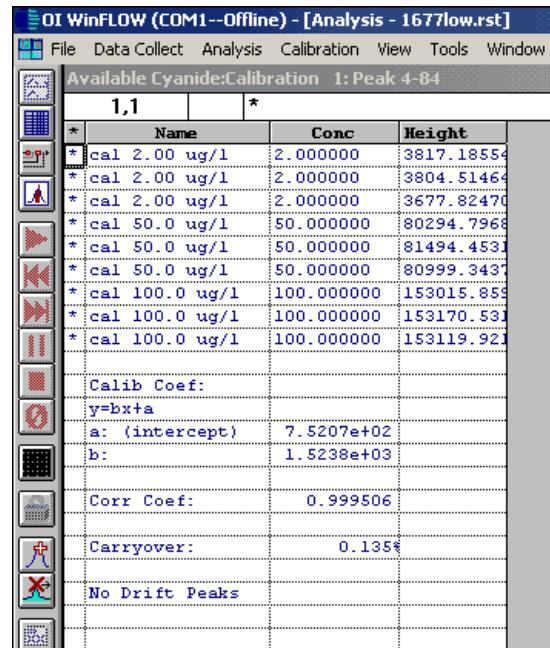


Figure 11. Available cyanide calibration results (2.0–100 µg/L)