Method Abstract

Scope

This method is used for the determination of nitrate (NO_3^-) plus nitrite (NO_2^-) or nitrite singly in drinking water, groundwater, surface water, and domestic and industrial wastes according to USEPA Method 353.2 and Standard Methods 4500–NO_3^- F. Additionally, this method enables nitrate plus nitrite according to ISO Method 13395. Also, this method can be used to analyze nitrate plus nitrite in 2M potassium chloride (KCl) extracts of soils and plants.

Summary

Cadmium metal reduces nitrate quantitatively to nitrite. Nydahl provides a good discussion of nitrate reduction by cadmium metal. The nitrite formed, in addition to any nitrite originally present in the sample, is diazotized with sulfanilamide and is subsequently coupled with *N*-(1-naphthyl)ethylenediamine dihydrochloride. The resulting highly colored azo dye is colorimetrically detected at 540 nm. A calibration curve allows accurate quantitation of the detected nitrite.

Measure nitrite singly by performing the same analysis as in described before but without cadmium reduction; without cadmium, nitrate is not reduced to nitrite and is not detected since only nitrite forms the azo dye.

Interferences

Turbid samples may interfere with the photometric detector's ability to measure the true absorbance of the sample. Filter turbid samples prior to analysis.

Iron, copper, and other metals may interfere with the analysis by binding with the nitrate and/or nitrite in the sample, thus blocking the color formation reaction. Use of EDTA or other complexing agents in the buffering solution manages this interference.

Samples that are outside the functional pH range of the buffering solution may affect the results obtained from this method. Adjust the pH of these samples to within a range of 5-9 using either concentrated hydrochloric acid (HCl) or sodium hydroxide (NaOH).

Oil and grease will coat the cadmium surface, thus reducing its reduction efficiency. Extract samples containing large concentrations of oil and grease with an appropriate organic solvent.

Sulfide in the presence of cadmium will form cadmium sulfide (CdS), which will inhibit nitrate reduction. Samples containing sulfide cannot be determined using this method without first removing the sulfide by precipitation with cadmium salts.

Dissolved oxygen and carbonate can react with the cadmium to form cadmium hydroxide ($Cd(OH)_2$) and cadmium carbonate ($CdCO_3$) precipitants. Additionally, dissolved oxygen competitively inhibits the reduction of nitrate to nitrite. Care must be taken to ensure that the pH never exceeds 8.5. Also, degas all reagents prior to analysis.

Chlorine may reduce the reduction efficiency of the cadmium reactor. Samples that may contain residual chlorine should be tested for reduction efficiency through the analysis of Matrix Spike/Matrix Spike Duplicate (MS/MSD) samples (Section 9.3). When necessary, dechlorinate samples with sodium thiosulfate ($Na_2S_2O_3$).

Method interferences may be caused by contaminants in the reagents, reagent water, glassware, etc., which may bias the results. Care should be taken to keep all such items free of contaminants.

Norwitz and Keliher, as well as Nydahl, have compiled a comprehensive study of interferences in the spectrophotometric analysis of nitrite.

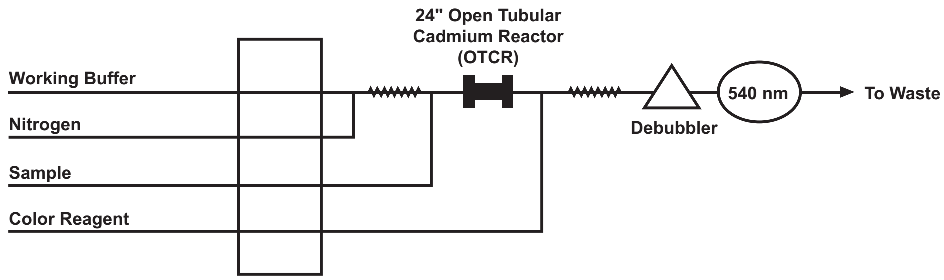
Performance Specifications

Range:	0.005–10.0 mg/L
Throughput:	55 samples/hour
Precision (at 0.01 mg/L):	~4% RSD
Precision (at 0.1 mg/L):	<0.5% RSD
Precision (at 1.0 mg/L):	<1% RSD
Precision (at 10.0 mg/L):	<0.5% RSD
Method Detection Limit (MDL):	0.0005 mg/L
Accuracy:	108.88%
Cadmium Coil Reduction Efficiency:	96.03%

Chemicals

- Ammonium Chloride (low nitrate), NH_4Cl
- Ammonium Hydroxide, NH_4OH
- Brij®-35, 21% solution (part number A21-0110-33)
- Chloroform, HPLC Grade, $CHCl_3$
- Cupric Sulfate Pentahydrate, $CuSO_4 \bullet 5H_2O$
- Deionized (DI) Water, ASTM Type I or II
- Ethylenediaminetetraacetic Acid, Disodium Salt Dihydrate (EDTA), $C_{10}H_{16}N_2Na_2O_8 \bullet 2H_2O$
- Hydrochloric Acid, concentrated, HCl
- Imidazole, $C_3H_4N_2$
- *N*-(1-naphthyl)ethylenediamine dihydrochloride, $C_{12}H_{14}N_2 \bullet 2HCl$
- Phosphoric Acid, concentrated, H_3PO_4
- Potassium Nitrate, KNO_3
- Potassium Nitrite, KNO_2
- Sulfanilamide, $C_6H_8N_2O_2S$

Basic Flow Diagram



Selected Reference

Methods for the Determination of Inorganic Substances in Environmental Samples; EPA/600/R-93/100; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory: Cincinnati, OH, 1993; Method 353.2.

Norwitz, G.; Keliher, P.N. Study of Interferences in the Spectrophotometric Determination of Nitrite Using Composite Diazotization-Coupling Reagents. *Analyst* **1985**, *110*, 689–694.

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Nydahl, F. *Talanta* **1976**, *23*, 349–357.

Water Quality–Determination of Nitrate Nitrogen and Nitrate Nitrogen and the Sum of Both by Flow Analysis (CFA and FIA) and Spectrophotometric Detection. *International Standard*. ISO 13395:1996 (E); 1st ed. Geneva, Switzerland, 1996

Figures

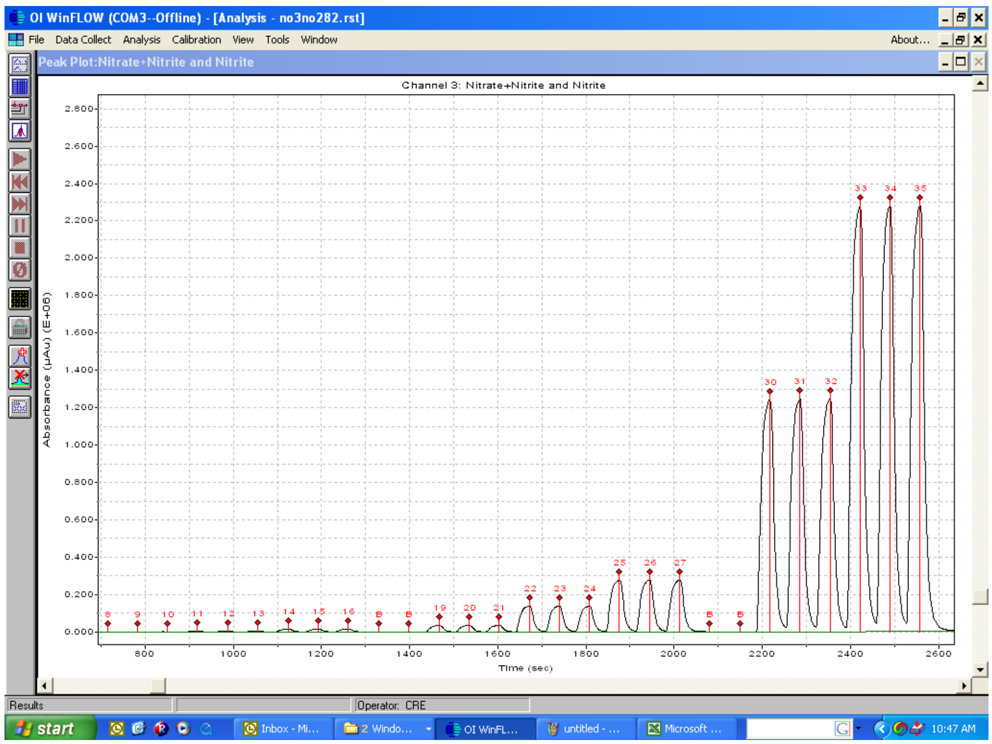

Figure 1. Nitrate Calibration (0.005–10.0 ppm)

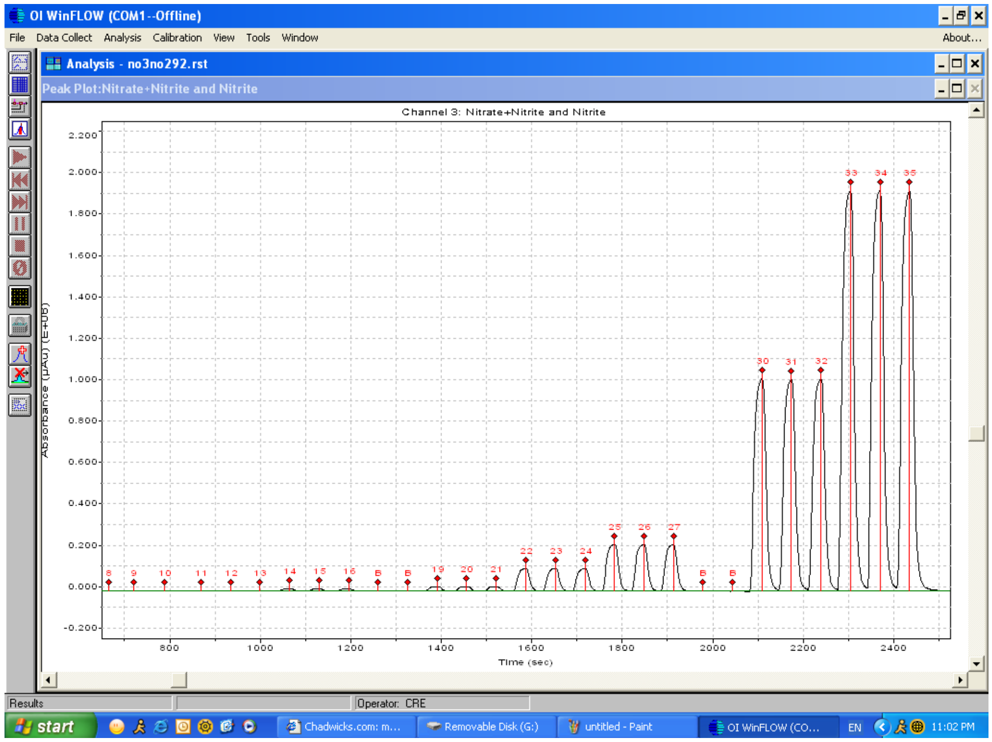

Figure 2. Nitrite Nitrogen Calibration (0.005–10.0 ppm)

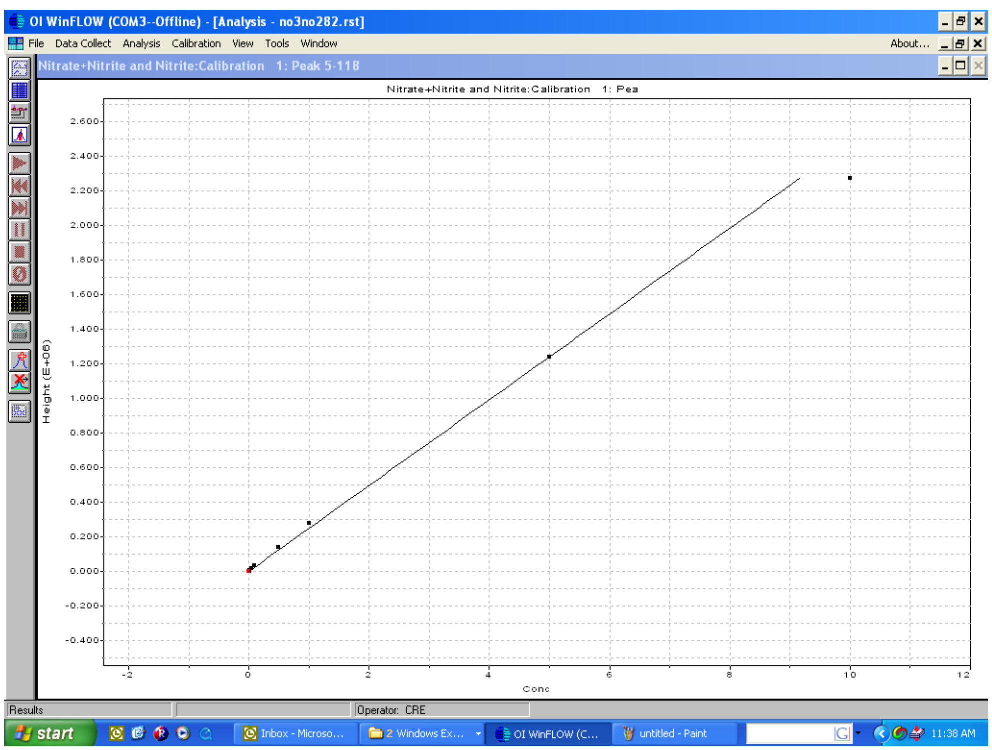

Figure 3. Nitrate Calibration Curve (0.005–10.0 ppm)

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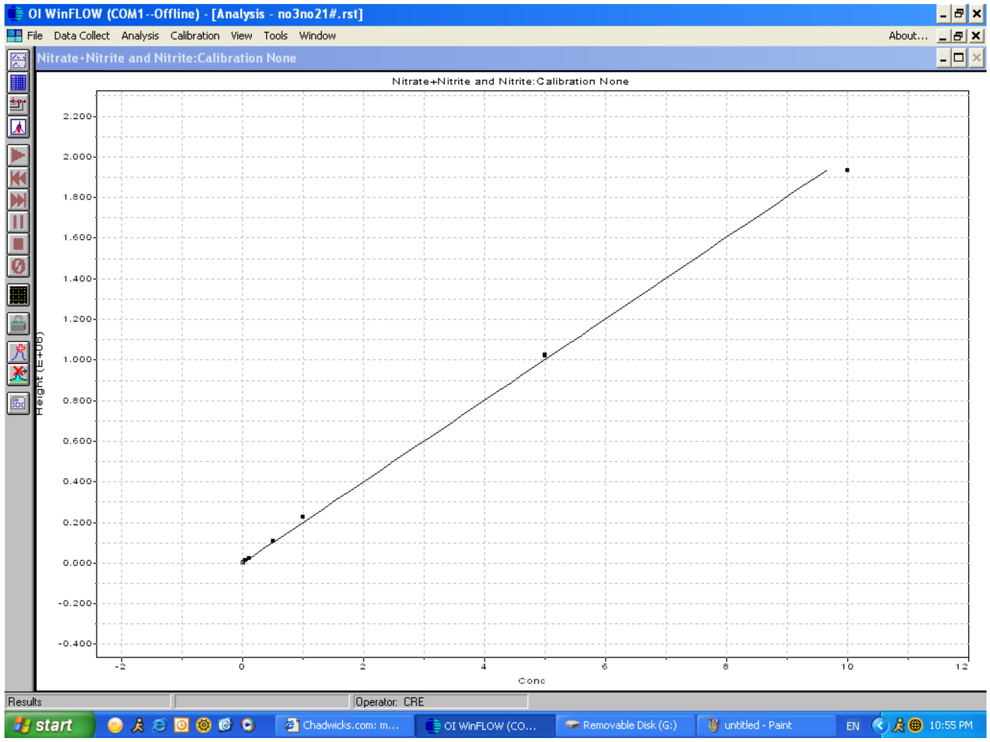

Figure 4. Nitrite Nitrogen Calibration Curve(0.005–10.0 ppm)

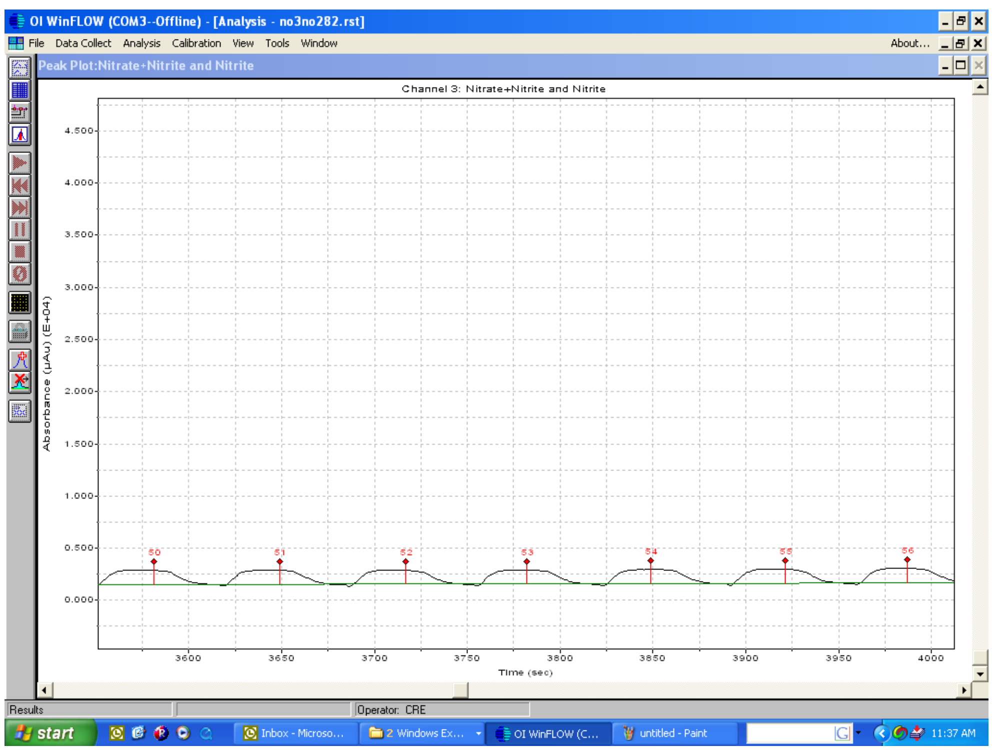

Figure 5. Nitrate Method Detection Limit (at 0.005 ppm)

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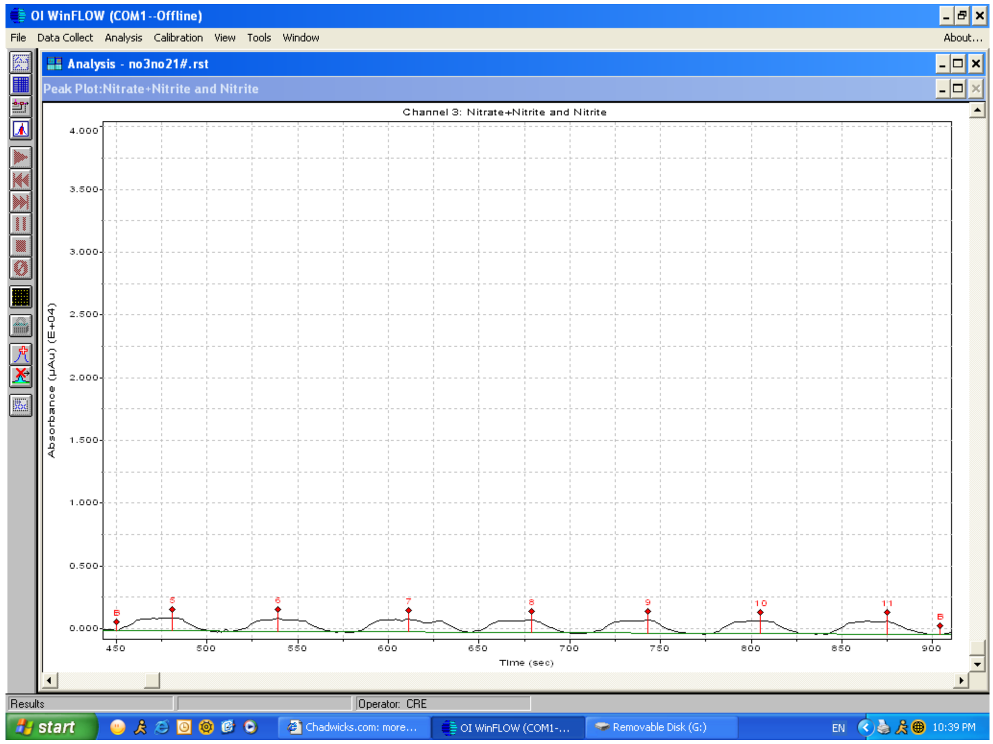

Figure 6. Nitrite Nitrogen Method Detection Limit (at 0.005 ppm)

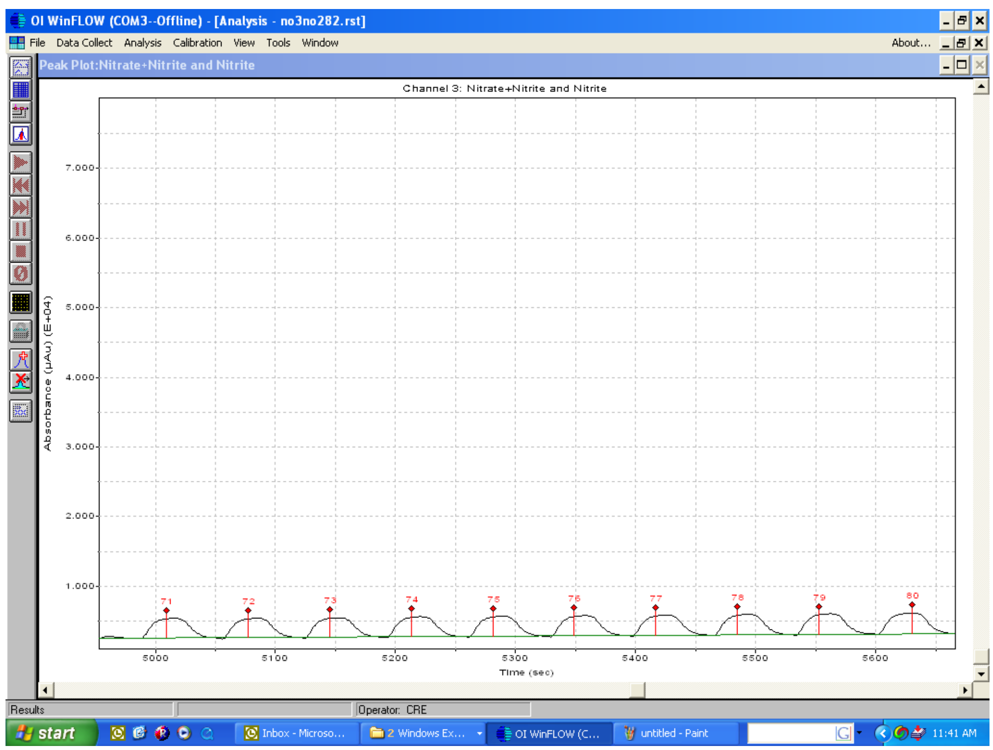

Figure 7. Nitrate Precision (at 0.01 ppm)

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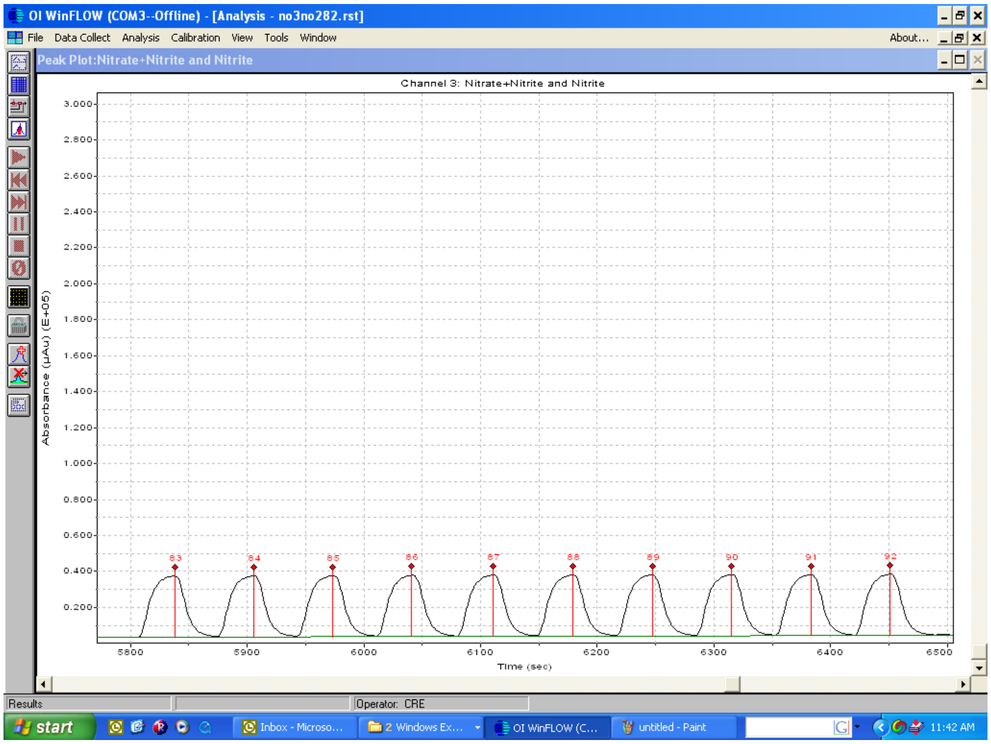

Figure 8. Nitrate Precision (at 0.10 ppm)

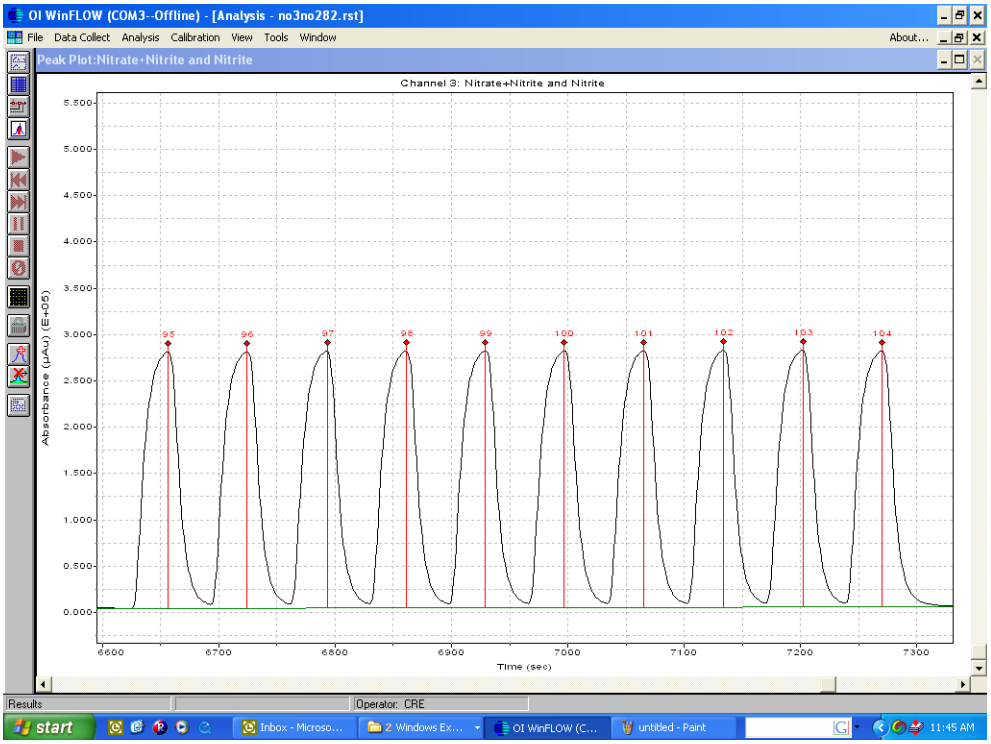

Figure 9. Nitrate Precision (at 1.0 ppm)

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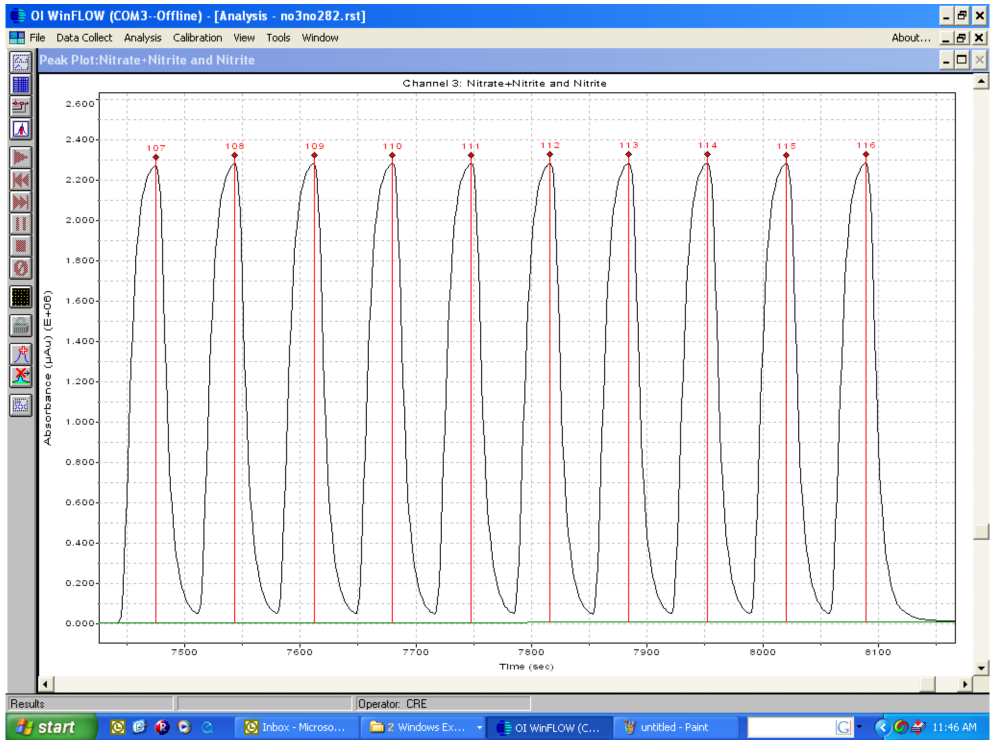

Figure 10. Nitrate Precision (at 10.0 ppm)

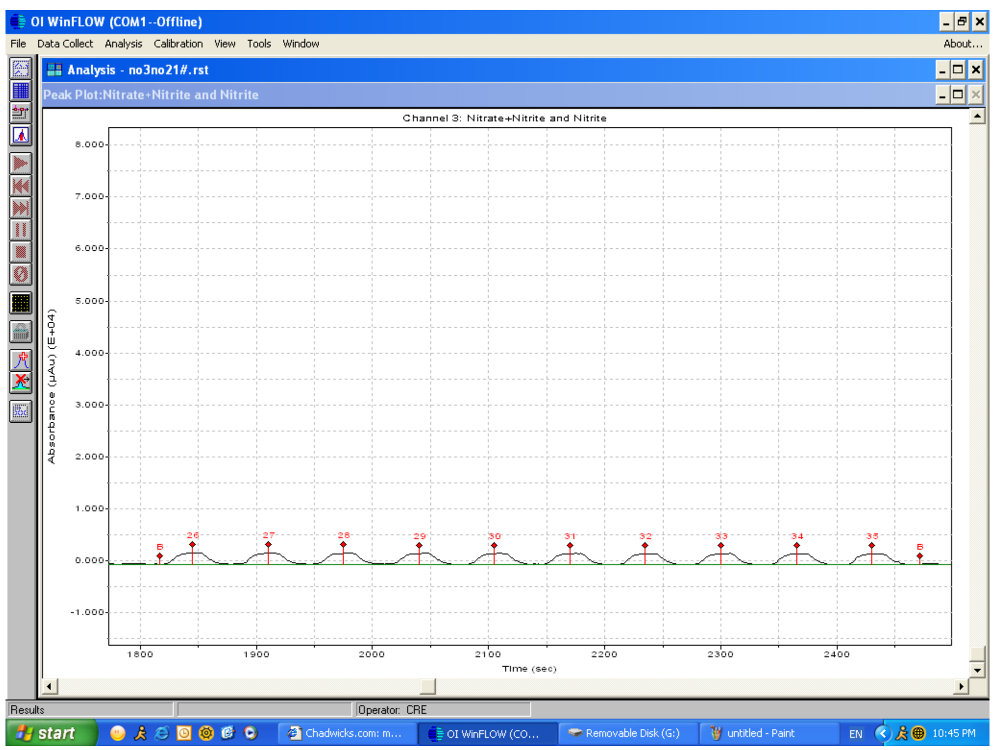

Figure 11. Nitrite Nitrogen Precision (at 0.01 ppm)

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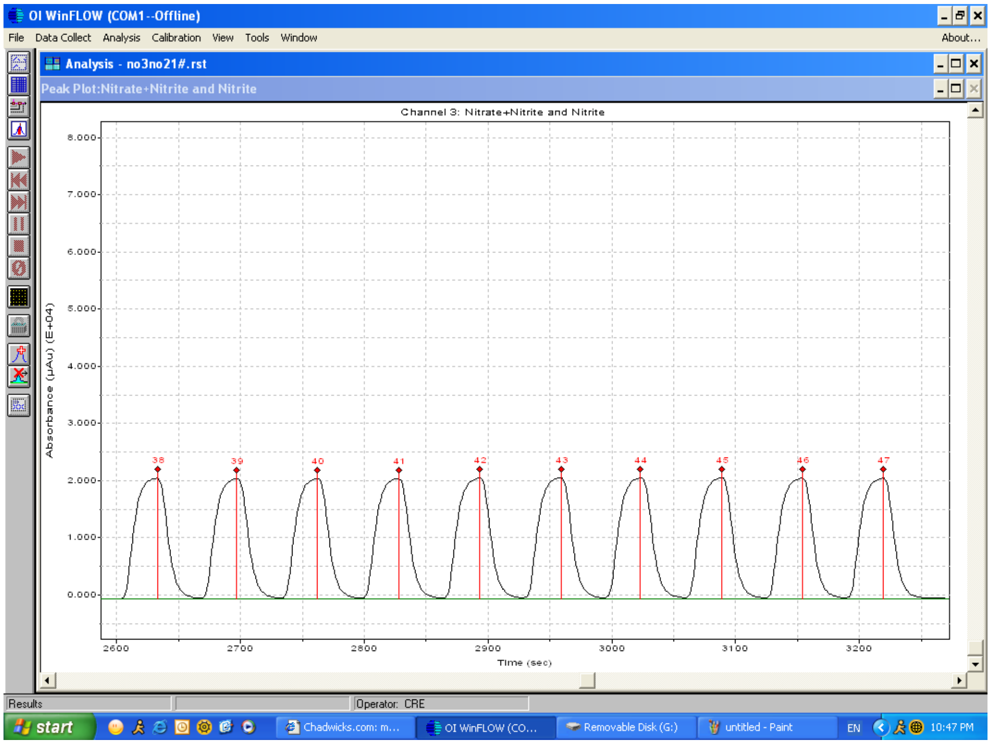

Figure 12. Nitrite Nitrogen Precision (at 0.1 ppm)

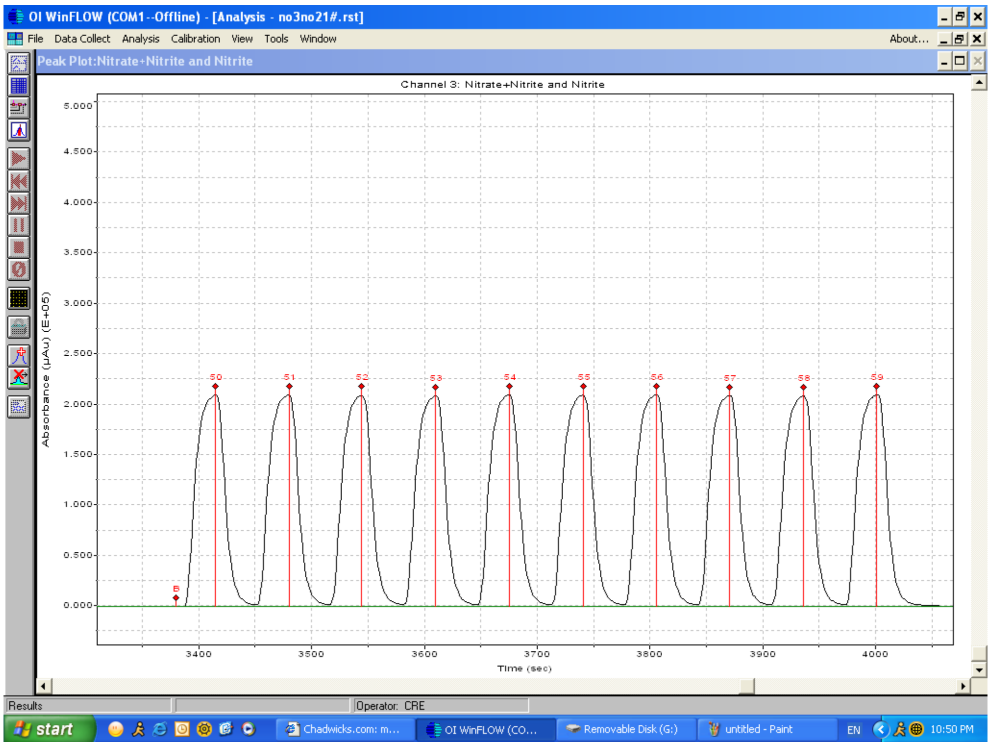

Figure 13. Nitrite Nitrogen Precision (at 1.0 ppm)

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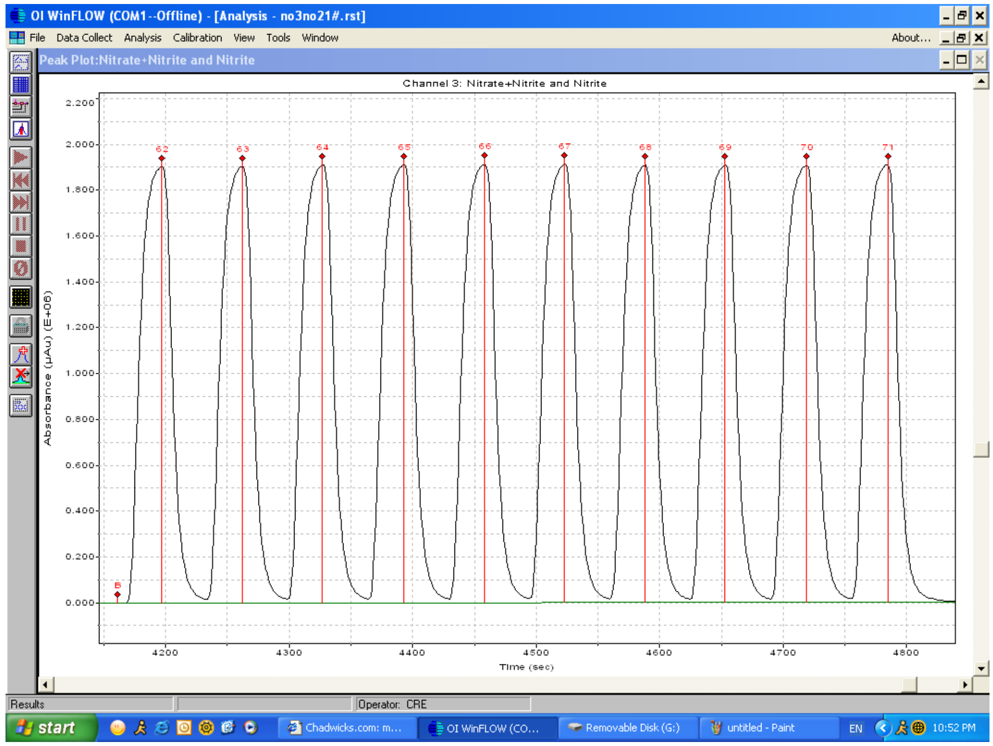

Figure 14. Nitrite Nitrogen Precision (at 10.0 ppm)

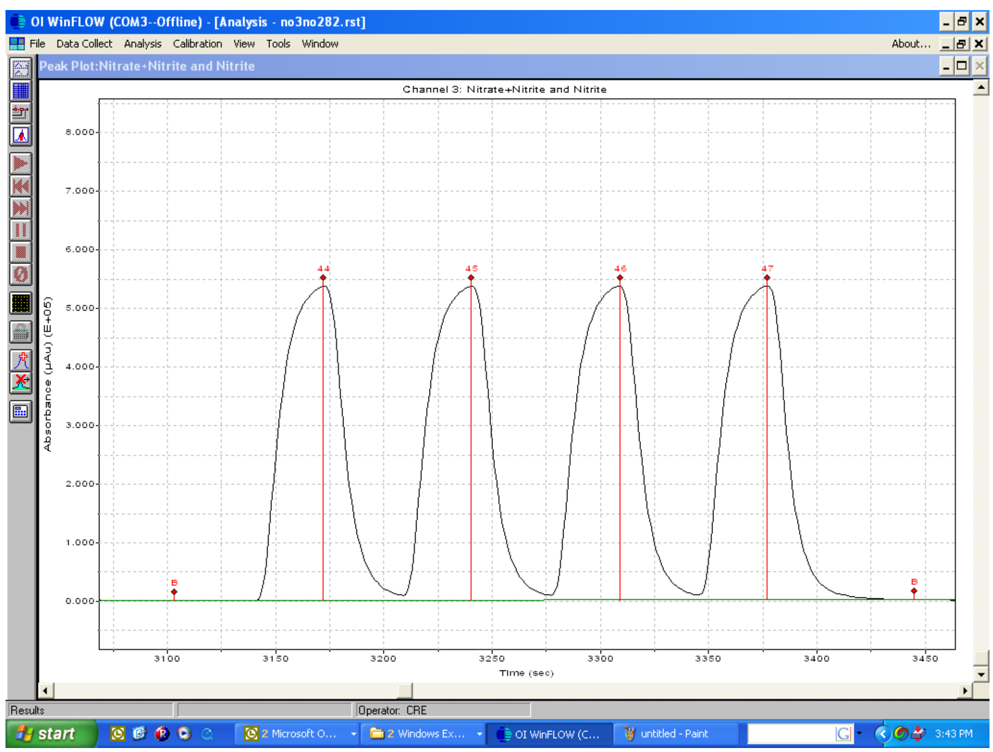

Figure 15. Nitrate plus Nitrite Nitrogen ERA QC Sample Precision (ERA 1.98 ppm)

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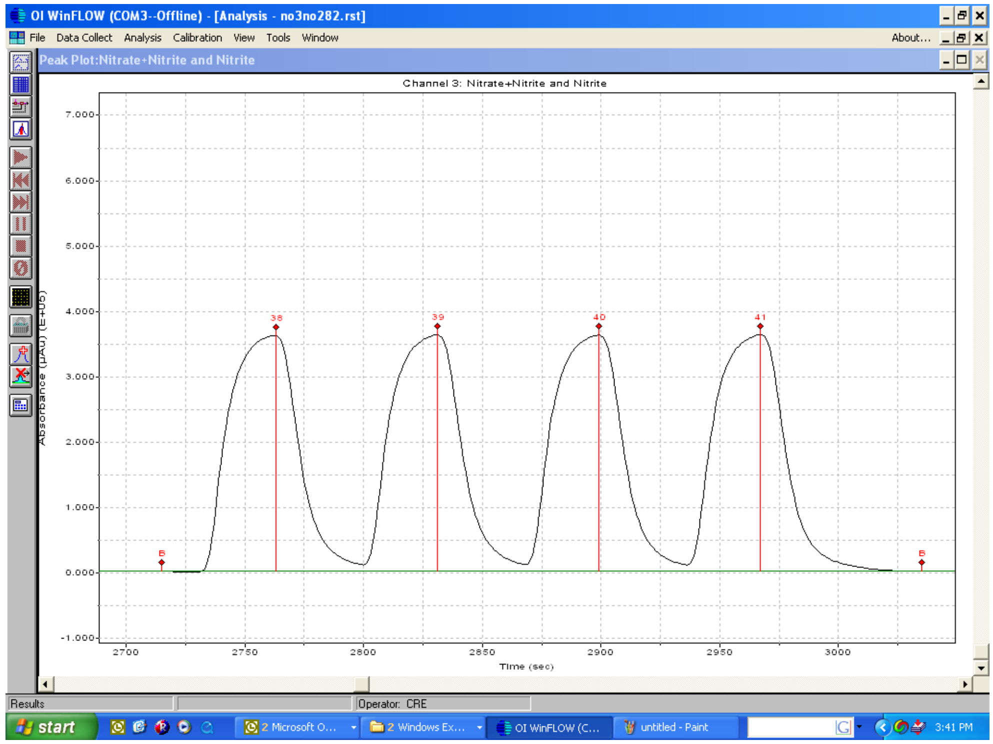
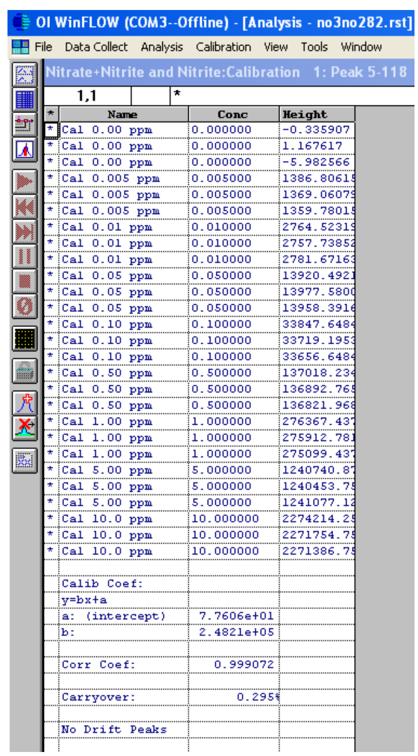
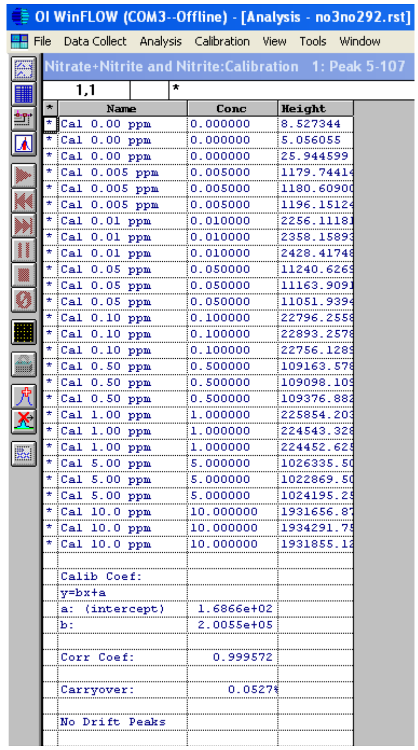


Figure 16. Nitrate plus Nitrite Nitrogen ERA QC Sample Precision
(2 M KCl extract 1.4 ppm)



*	Name	Conc	Height
*	Cal 0.00 ppm	0.000000	-0.335907
*	Cal 0.00 ppm	0.000000	1.167617
*	Cal 0.00 ppm	0.000000	-5.982566
*	Cal 0.005 ppm	0.005000	1386.8061
*	Cal 0.005 ppm	0.005000	1369.0607
*	Cal 0.005 ppm	0.005000	1359.7801
*	Cal 0.01 ppm	0.010000	2764.5231
*	Cal 0.01 ppm	0.010000	2757.7385
*	Cal 0.01 ppm	0.010000	2781.6716
*	Cal 0.05 ppm	0.050000	13920.492
*	Cal 0.05 ppm	0.050000	13977.580
*	Cal 0.05 ppm	0.050000	13958.391
*	Cal 0.10 ppm	0.100000	33847.648
*	Cal 0.10 ppm	0.100000	33719.195
*	Cal 0.10 ppm	0.100000	33656.648
*	Cal 0.50 ppm	0.500000	137018.23
*	Cal 0.50 ppm	0.500000	136892.76
*	Cal 0.50 ppm	0.500000	136821.96
*	Cal 1.00 ppm	1.000000	276367.43
*	Cal 1.00 ppm	1.000000	275912.78
*	Cal 1.00 ppm	1.000000	275099.43
*	Cal 5.00 ppm	5.000000	1240740.8
*	Cal 5.00 ppm	5.000000	1240453.7
*	Cal 5.00 ppm	5.000000	1241077.1
*	Cal 10.0 ppm	10.000000	2274214.2
*	Cal 10.0 ppm	10.000000	2271754.7
*	Cal 10.0 ppm	10.000000	2271386.7
	Calib Coef:		
	y=bx+a		
	a: (intercept)	7.7606e+01	
	b:	2.4821e+05	
	Corr Coef:	0.999072	
	Carryover:	0.295%	
	No Drift Peaks		

Figure 17. Nitrate Calibration Results (0.005–10.0 ppm)



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Nitrate+Nitrite and Nitrite:Calibration 1: Peak 5-107

1,1 *

*	Name	Conc	Height
*	Cal 0.00 ppm	0.000000	8.527344
*	Cal 0.00 ppm	0.000000	5.056055
*	Cal 0.00 ppm	0.000000	25.944599
*	Cal 0.005 ppm	0.005000	1179.7441
*	Cal 0.005 ppm	0.005000	1180.6090
*	Cal 0.005 ppm	0.005000	1196.1512
*	Cal 0.01 ppm	0.010000	2256.1118
*	Cal 0.01 ppm	0.010000	2358.1589
*	Cal 0.01 ppm	0.010000	2428.4174
*	Cal 0.05 ppm	0.050000	11240.626
*	Cal 0.05 ppm	0.050000	11163.909
*	Cal 0.05 ppm	0.050000	11051.939
*	Cal 0.10 ppm	0.100000	22796.255
*	Cal 0.10 ppm	0.100000	22893.257
*	Cal 0.10 ppm	0.100000	22756.128
*	Cal 0.50 ppm	0.500000	109163.57
*	Cal 0.50 ppm	0.500000	109098.10
*	Cal 0.50 ppm	0.500000	109376.88
*	Cal 1.00 ppm	1.000000	225854.20
*	Cal 1.00 ppm	1.000000	224543.32
*	Cal 1.00 ppm	1.000000	224452.62
*	Cal 5.00 ppm	5.000000	1026335.5
*	Cal 5.00 ppm	5.000000	1022869.5
*	Cal 5.00 ppm	5.000000	1024195.2
*	Cal 10.0 ppm	10.000000	1931656.8
*	Cal 10.0 ppm	10.000000	1934291.7
*	Cal 10.0 ppm	10.000000	1931855.1
	Calib Coef:		
	y=bx+a		
	a: (intercept)	1.6866e+02	
	b:	2.0055e+05	
	Corr Coef:	0.999572	
	Carryover:	0.0527%	
	No Drift Peaks		

Figure 18. Nitrite Nitrogen Calibration Results (0.005–10.0 ppm)

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Table 1. Nitrate plus Nitrite Nitrogen and Nitrite Nitrogen Method Data

Parameter	Calibrant 0.005 mg/L	Calibrant 0.01 mg/L	Calibrant 0.1 mg/L	Calibrant 1.0 mg/L	Calibrant 10.0 mg/L	ERA QC Standard 1.98 mg/L	2 M KCl Soil Extract QC Standard 1.4 mg/L
Rep 1	0.0051	0.0106	0.1367	1.1135	9.1328	2.1610	1.4551
Rep 2	0.0050	0.0101	0.1366	1.1110	9.1391	2.1549	1.4545
Rep 3	0.0051	0.0103	0.1364	1.1118	9.1330	2.1540	1.4525
Rep 4	0.0050	0.0105	0.1369	1.1112	9.1398	2.1531	1.4540
Rep 5	0.0051	0.0105	0.1368	1.1122	9.1356	—	—
Rep 6	0.0052	0.0106	0.1367	1.1118	9.1429	—	—
Rep 7	0.0053	0.0107	0.1370	1.1118	9.1456	—	—
Rep 8	—	0.0108	0.1363	1.1143	9.1400	—	—
Rep 9	—	0.0109	0.1366	1.1117	9.1296	—	—
Rep 10	—	0.0118	0.1368	1.1091	9.1452	—	—
Average	0.0051	0.0107	0.1367	1.1118	9.1384	2.1557	1.4540
Standard Deviation	0.0001	0.0004	0.0002	0.0014	0.0055	0.0036	0.0011
% RSD	1.99	4.08	0.15	0.13	0.06	0.17	0.08
MDL	0.0003	—	—	—	—	—	—
% Accuracy	—	—	—	—	—	108.89%	103.88%

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