Scope

This method is used for determining 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^-. Additionally, this method enables nitrate plus nitrite analysis according to ISO Method 13395. Also, this method can be used to analyze nitrate plus nitrite in 2 M potassium chloride (KCl) extract of soils and plants.

Summary

Quantitatively reduce nitrate to nitrite using cadmium metal. Nydahl provides a good discussion of nitrate reduction by cadmium metal. Diazotize the formed nitrite in addition to any nitrite originally present in the sample with sulfanilamide and subsequently couple with *N*-(1-naphthyl)ethylenediamine dihydrochloride. Colorimetrically detect the resulting highly colored azo dye at 540 nm. A calibration curve allows accurate quantitation of the detected nitrite.

Measure nitrite singly by performing the same analysis as described previously but without the cadmium reduction. Nitrate is not reduced to nitrite without cadmium and is not detected since only nitrite forms the azo dye.

Interferences

Filter turbid samples prior to analysis.

Ethylenediaminetetraacetic acid (EDTA) is added to eliminate interferences from iron, copper, or other metals.

Samples that are outside the functional pH range of the ammonium chloride buffer 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 ammonium hydroxide (NH_4OH).

Oil and grease coat the cadmium surface, reducing its reduction efficiency; extract samples containing large oil and grease concentrations with an appropriate organic solvent.

Sulfide in the presence of cadmium forms cadmium sulfide (CdS), which precipitates from solution;samplescontainingsulfidecannotbedeterminedbythism
method without first removing the sulfide by precipitating with cadmium salts.

Chlorine reduces the cadmium reactor's reduction efficiency; dechlorinate samples with sodium thiosulfate ($Na_2S_2O_3$).

Method interferences caused by contaminants in the reagents, reagent water, glassware, etc., may bias the results; take appropriate precautions to keep all such items free of contaminants. See Norwitz and Keliher for a comprehensive study of interferences in the spectrophotometric analysis of nitrite.

Performance Specifications

Range:	0.01–10 mg/L
Throughput:	60 samples/hour
Precision (at 0.1 mg/L):	~6% RSD
Precision (at 5.0 mg/L):	<1% RSD
Method Detection Limit (MDL):	0.001 mg/L

Analysis of QC Samples

Matrix	True Value	Acceptance Limit	Results	% RSD	n
Water ERA	19.8	17.4–22.4	20.4	0.524	4
Soil: 2 M KCl Extract	14	9–19	15.7	0.307	4
Soil: Water Extract	14	9–19	12.5	0.528	4

Chemicals

Ammonium Chloride, NH_4Cl

Ammonium Hydroxide, NH_4OH

Cadmium, Cd

Chloroform, $CHCl_3$

Cupric Sulfate Pentahydrate, $CuSO_4•5H_2O$

Ethylenediaminetetraacetic Acid, Disodium Salt Dihydrate (EDTA), $C_{10}H_{16}N_2Na_2O_8•2H_2O$

Hydrochloric Acid, concentrated, HCl

N-(1-naphthyl)ethylenediamine Dihydrochloride, $C_{12}H_{14}N_2•2HCl$

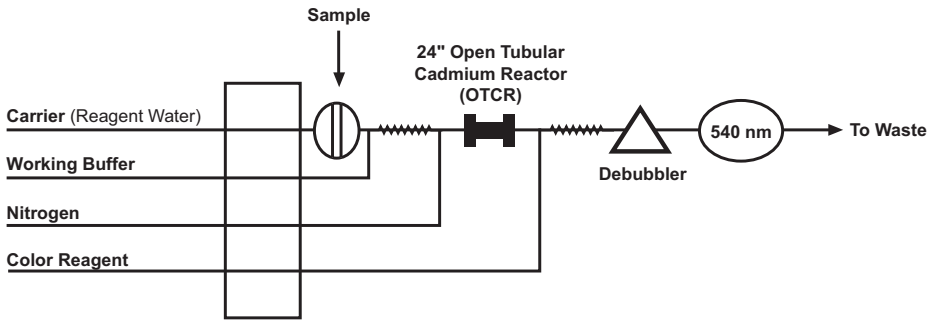
Phosphoric Acid, concentrated, H_3PO_4

Potassium Nitrate, KNO_3

Potassium Nitrite, KNO_2

Sulfanilamide, $C_6H_8N_2O_2S$

Basic Flow Diagram



Note

This method complies with USEPA Method 353.2.

Selected References

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.

Norwitz, G.; Keliher, P.N. Study of Interferences in the Spectrophotometric Determination of Nitrite Using Composite Diazotization-Coupling Reagents. *Analyst* **1986**, *111*, 1033–1037.

Standard Methods for the Examination of Water and Wastewater, 17th ed.; American Public Health Association: Washington, D.C., 1989; 4–178.

(800) 653-1711
(979) 690-1711
www.oico.com
oimail@oico.com

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

Figures

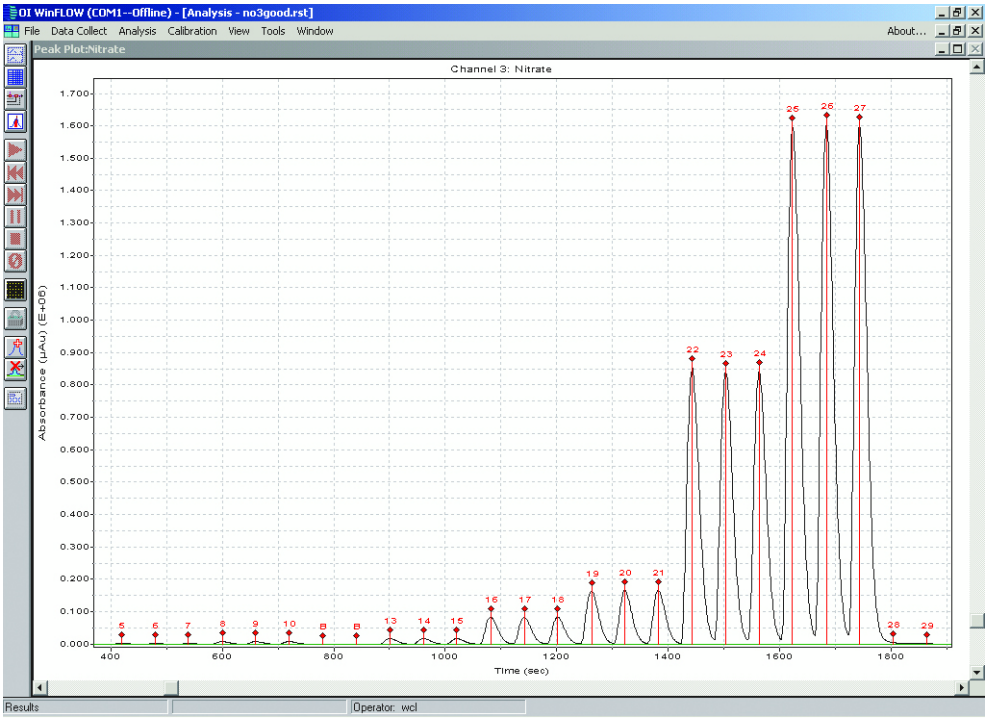


Figure 1. Nitrate plus Nitrite Calibration (0.01–10.0 ppm)

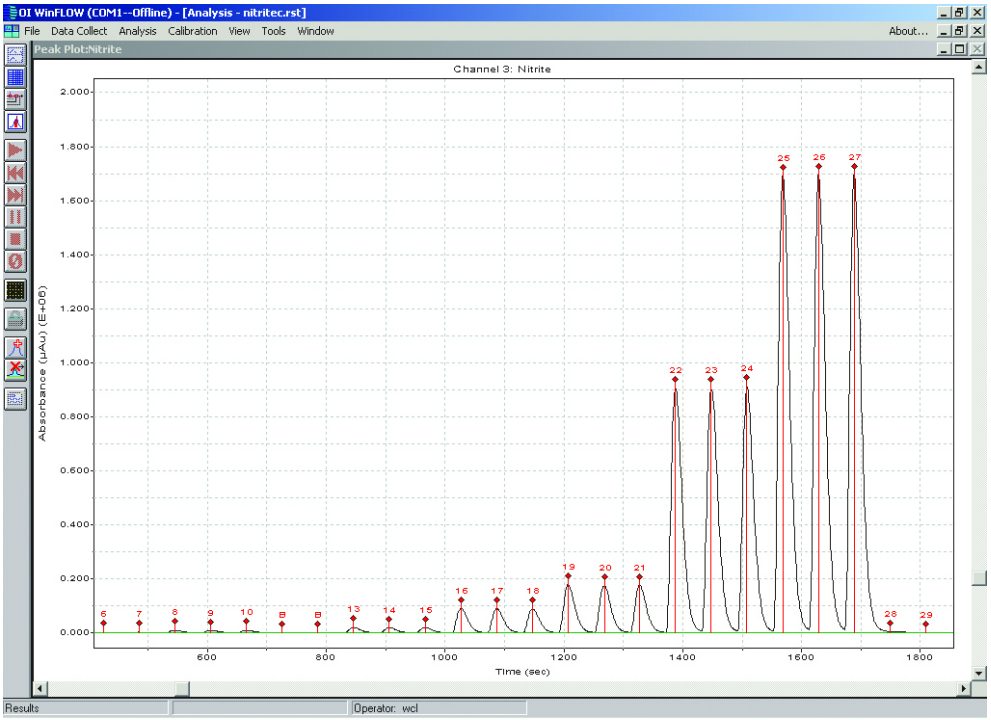


Figure 2. Nitrite Calibration (0.01–10.0 ppm)

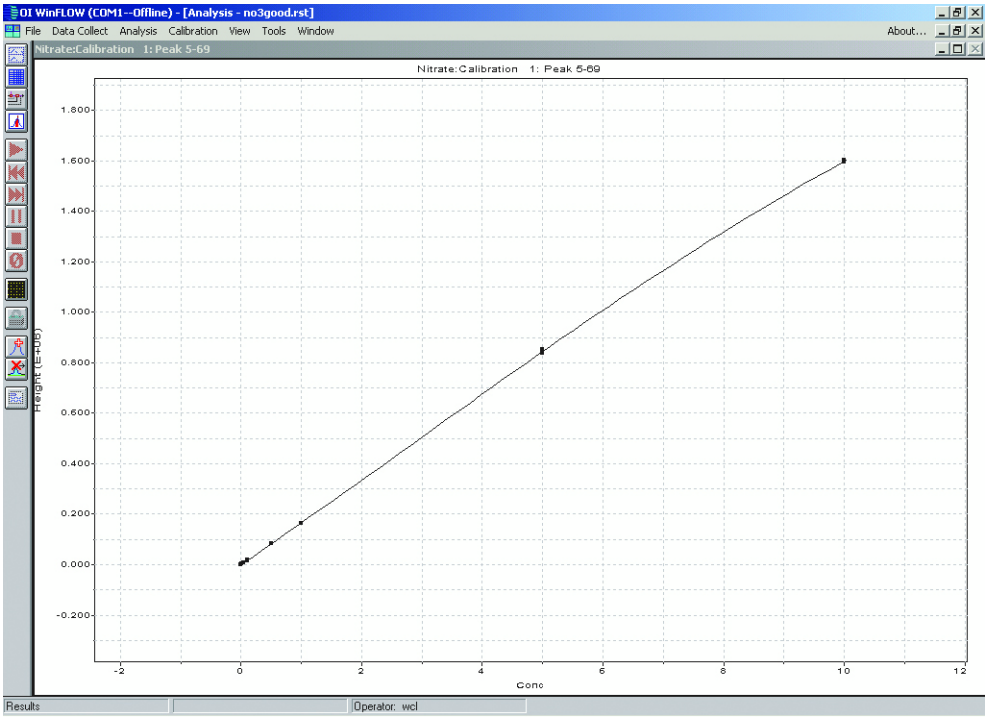


Figure 3. Nitrate plus Nitrite Calibration Curve (0.01–10.0 ppm)

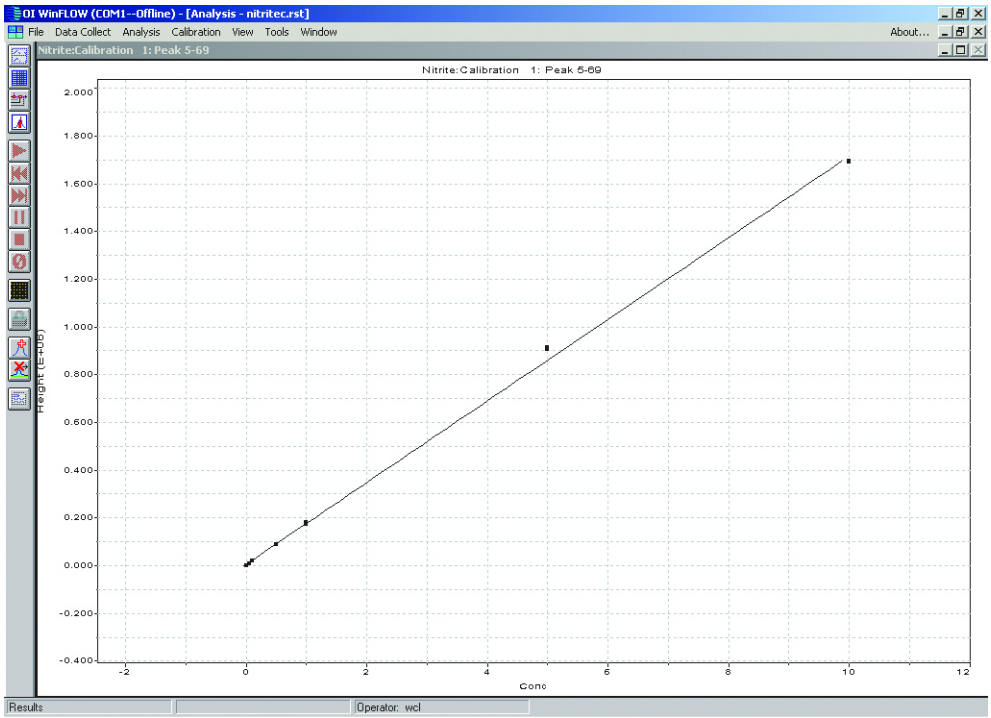


Figure 4. Nitrite Calibration Curve (0.01–10.0 ppm)

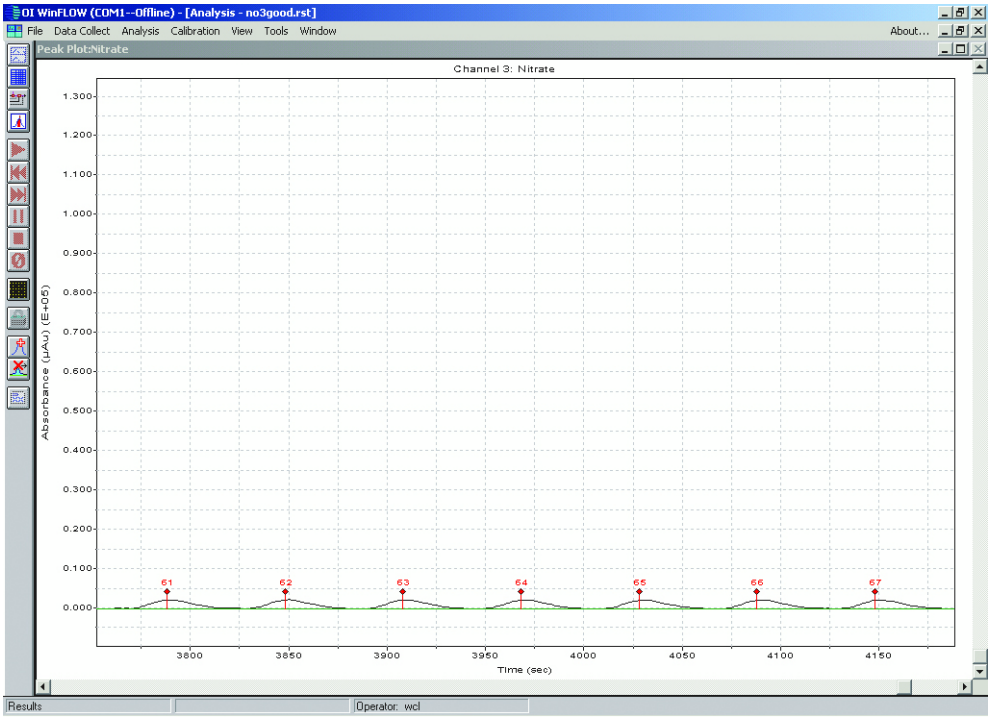


Figure 5. Nitrate plus Nitrite Method Detection Limit (at 0.01 ppm)

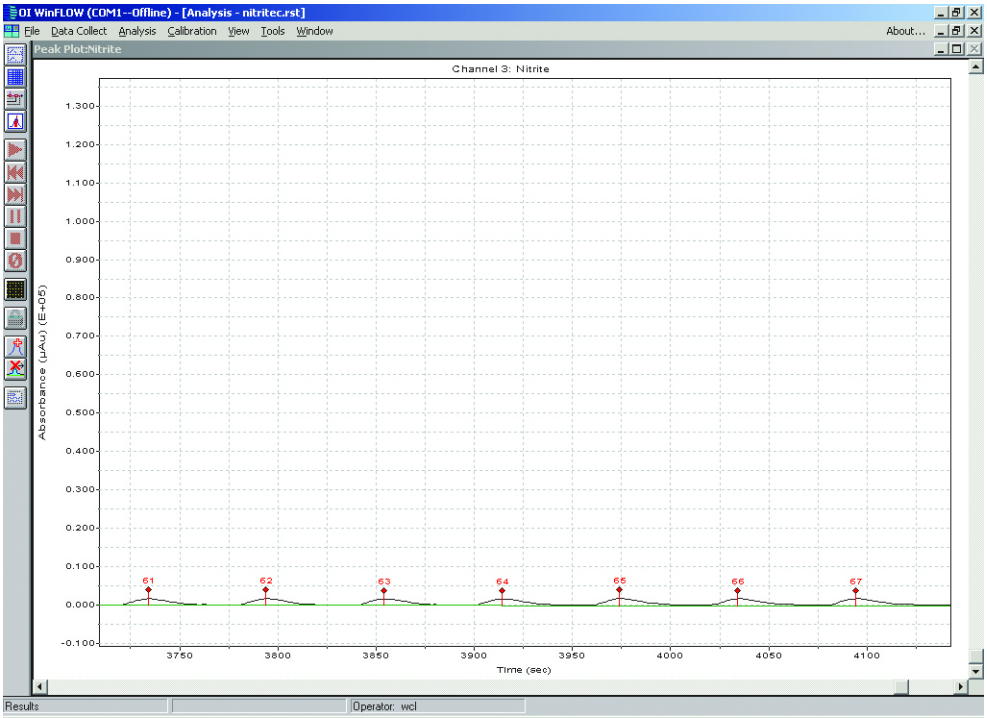


Figure 6. Nitrite Method Detection Limit (at 0.01 ppm)

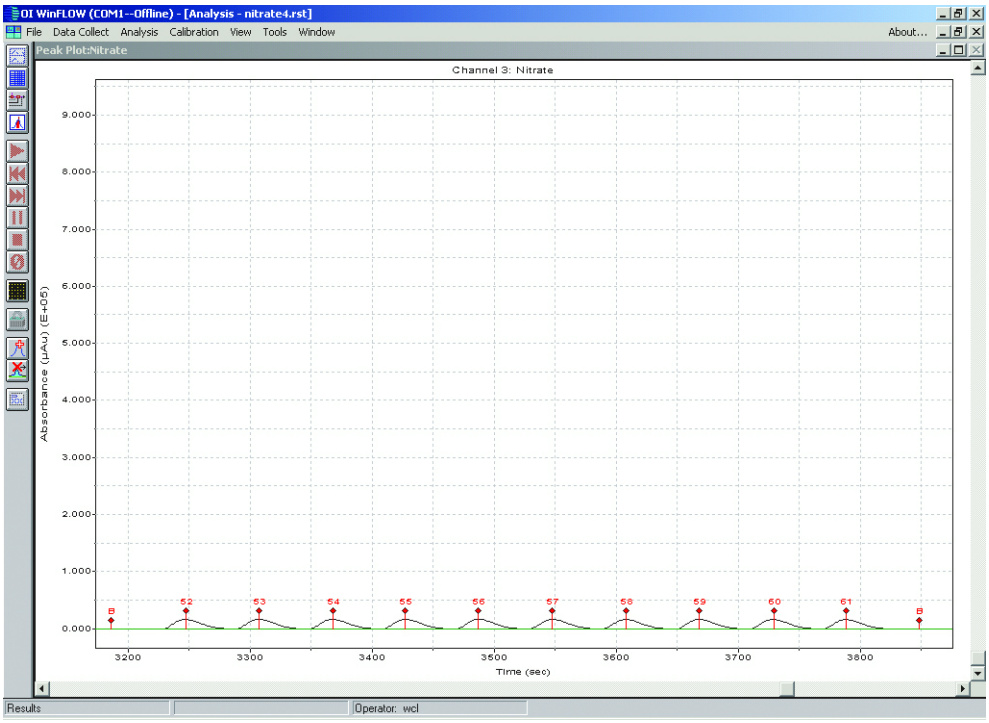


Figure 7. Nitrate plus Nitrite Precision (at 0.1 ppm)

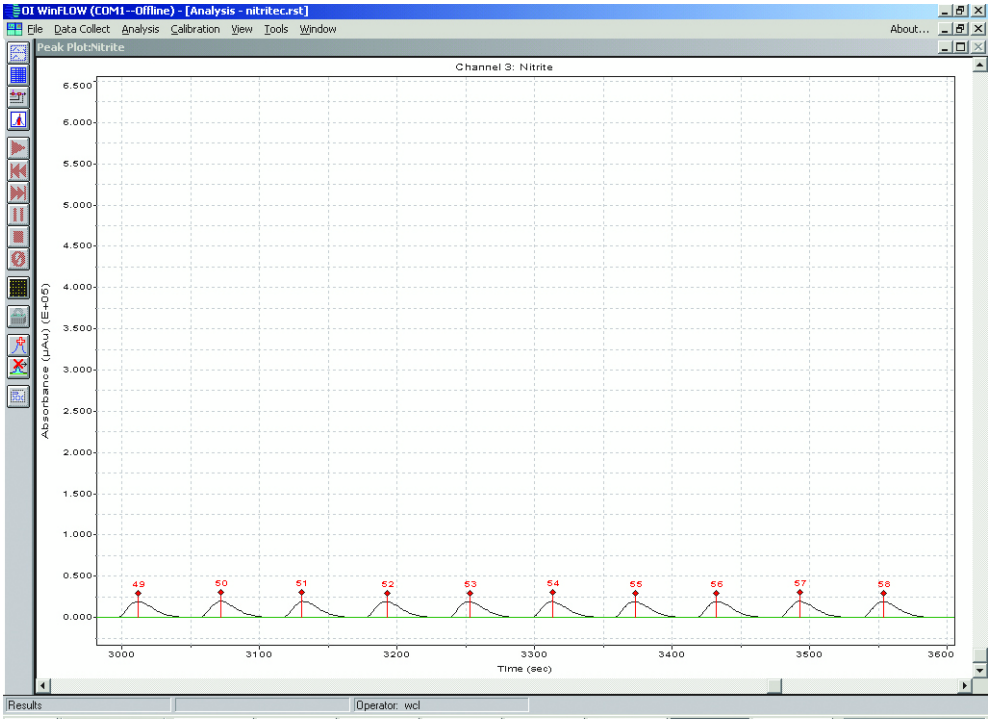


Figure 8. Nitrite Precision (at 0.1 ppm)

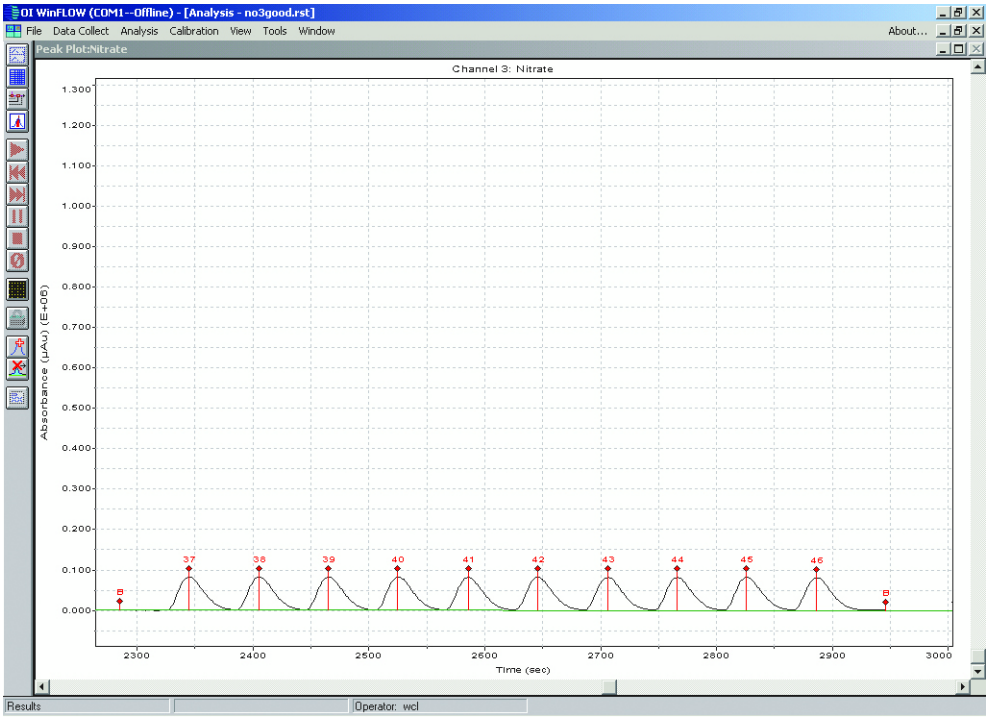


Figure 9. Nitrate plus Nitrite Precision (at 0.5 ppm)

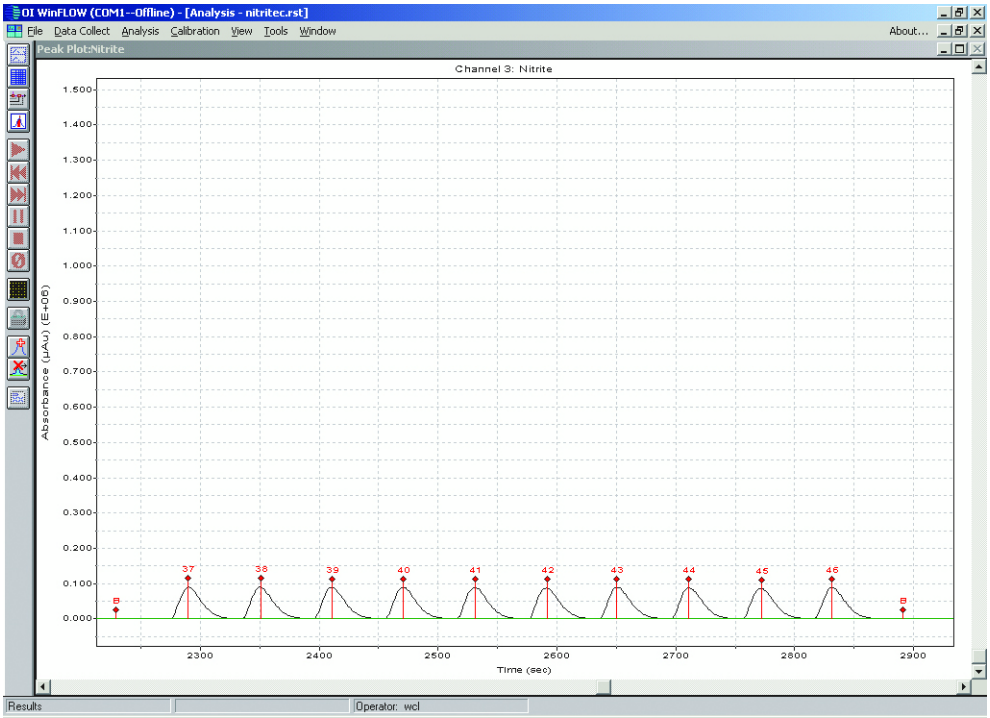


Figure 10. Nitrite Precision (at 0.5 ppm)

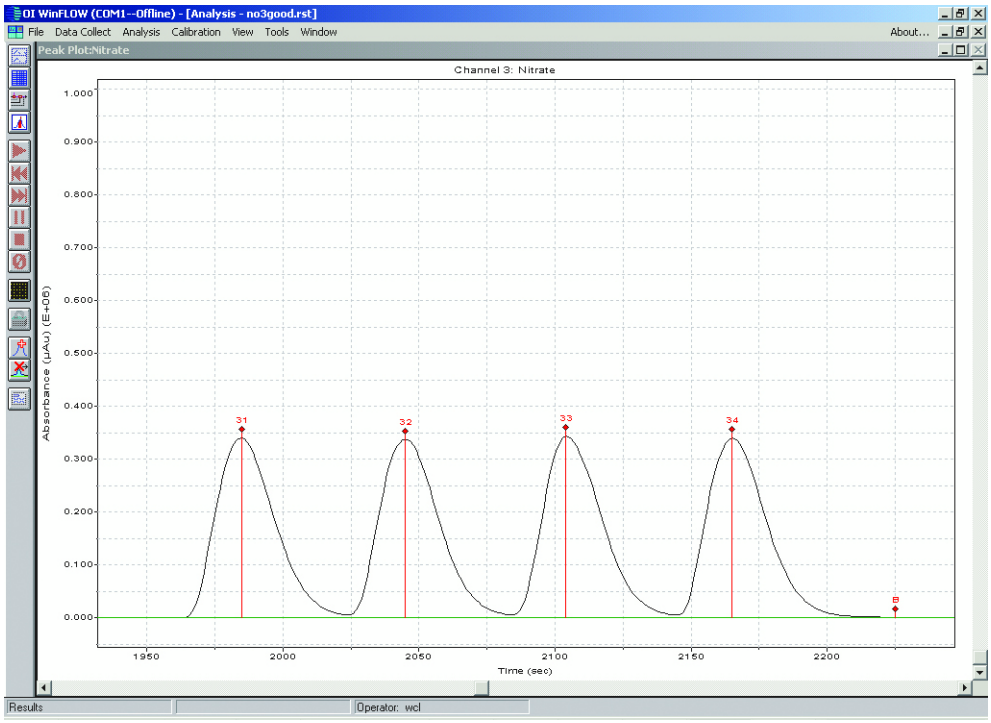


Figure 11. Nitrate plus Nitrite IDAC Replicates ERA 1.98 ppm NO_3

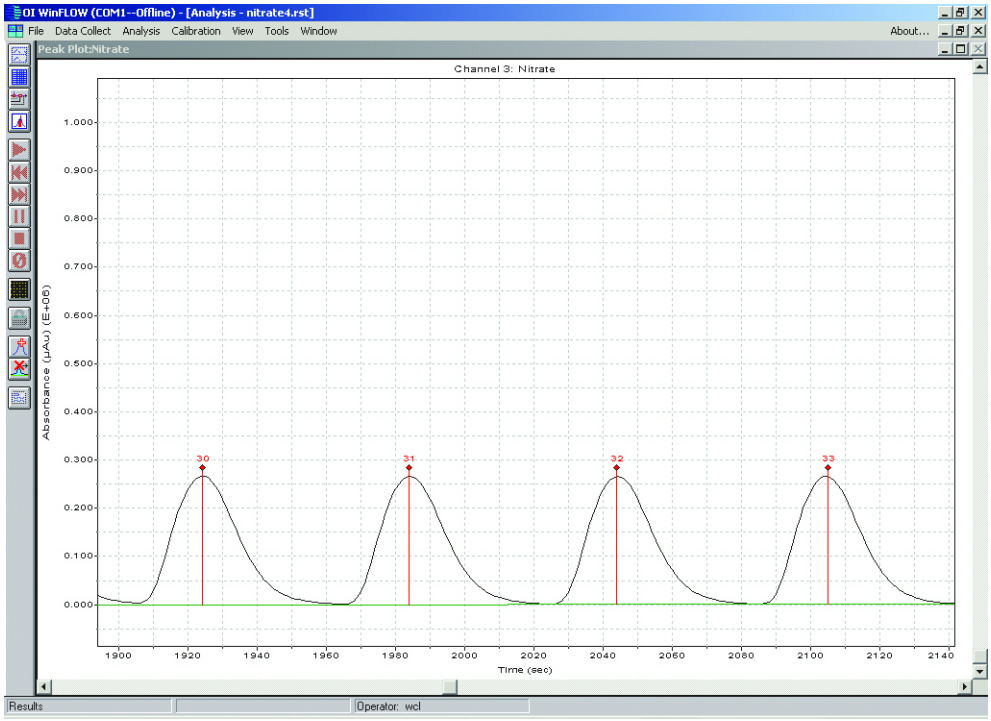


Figure 12. Nitrate plus Nitrite Precision (in 2M KCL Soil Extracts)

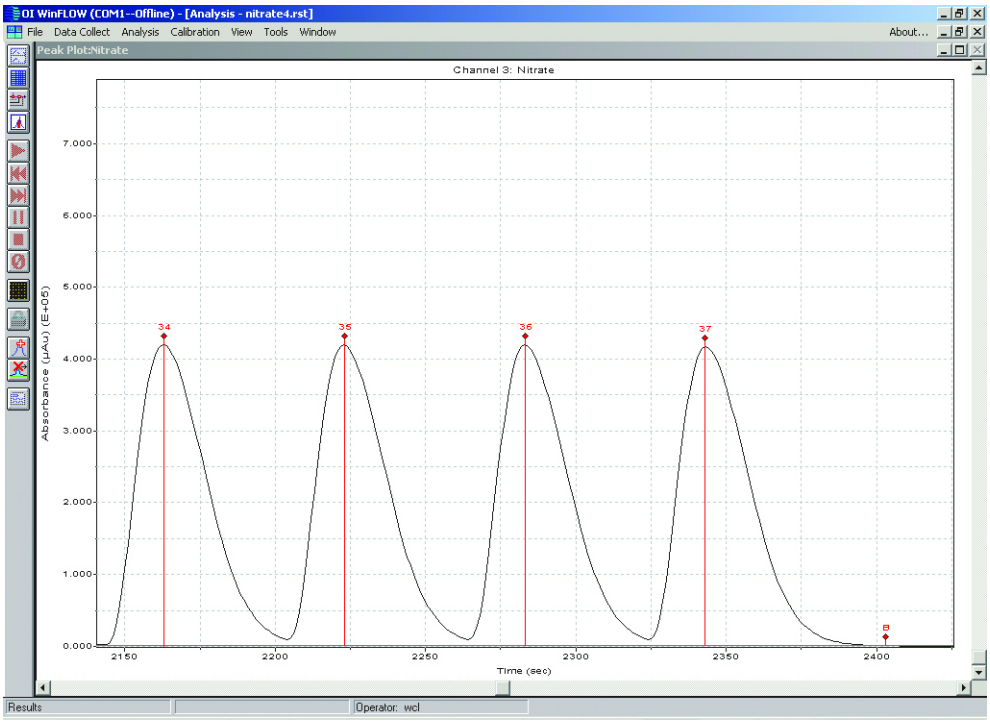


Figure 13. Nitrate plus Nitrite Precision (in Soil Water Extracts)

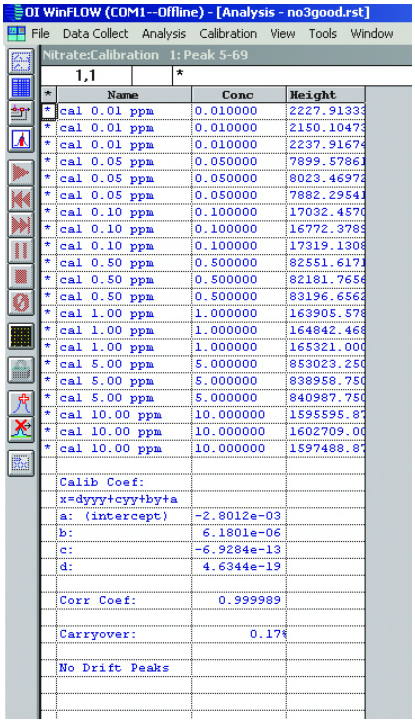


Figure 14. Nitrate plus Nitrite Calibration Results (0.01–10.0 ppm)

Table 1. Nitrate plus Nitrite Nitrogen Method Data

Parameter	Calibrant 0.010 mg N/L	Calibrant 0.100 mg N/L	Calibrant 0.500 mg N/L	AgroMAT AG-1 (2 M KCL)	ERA P127-739B
Rep 1	0.0108	0.102	0.505	15.8	20.4
Rep 2	0.0102	0.101	0.502	15.7	20.5
Rep 3	0.0101	0.100	0.501	15.7	20.4
Rep 4	0.0102	0.101	0.500	15.7	20.3
Rep 5	0.0098	0.101	0.498	—	—
Rep 6	0.0098	0.101	0.500	—	—
Rep 7	0.0103	0.117	0.493	—	—
Rep 8	—	0.101	0.493	—	—
Rep 9	—	0.102	0.498	—	—
Rep 10	—	0.117	0.490	—	—
Average	0.0102	0.104	0.498	15.7	20.4
Standard Deviation	0.000317	0.006709	0.004654	0.0485	0.1082
% RSD	3.12	6.43	0.93	0.31	0.53
% Recovery	102	104	99.6	112	103
MDL	0.001	—	—	—	—

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