Nitrate plus Nitrite Nitrogen or NItrite Nitrogen by Segmented Flow Analysis (SFA) or Flow Injection Analysis (FIA), USEPA 353.2

FLOW INJECTION ANALYSIS (FIA) & SEGMENTED FLOW ANALYSIS (SFA) SERIES

Cartridge Part Number: 331376CT (SFA) and 330093CT (FIA)
Channel Part Number: 331377 Channel - 3700 Nitrate/Nitrite SFA
                          330108 Channel - 3700 Nitrate (NO$_3$ Nitrite (NO$_2$ FIA)

Scope and Application

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 US EPA Method 353.2, Standard Methods 4500-NO$_3^-$I and 4500-NO$_3^-$F and ISO Method 13395.[1,2,3] This method includes information for both FIA and SFA.

Method Performance

Method Performance	SFA	FIA
Range	0.005 – 10 mg/L	0.005 – 10 mg/L
Rate	40 samples/hour	48 samples/hour
Precision	1% RSD at mid-point of range	1% RSD at mid-point of range
Method Detection Limit (MDL)	0.001 mg/L	0.001 mg/L

For SFA analysis, the range may be extended to analyze other concentrations by modifying the Load Time. For FIA analysis, this may be accomplished by changing the size of the sample loop.

Figure 1. General SFA Flow Diagram for Nitrate plus Nitrite Nitrogen and Nitrite Nitrogen by USEPA 353.2
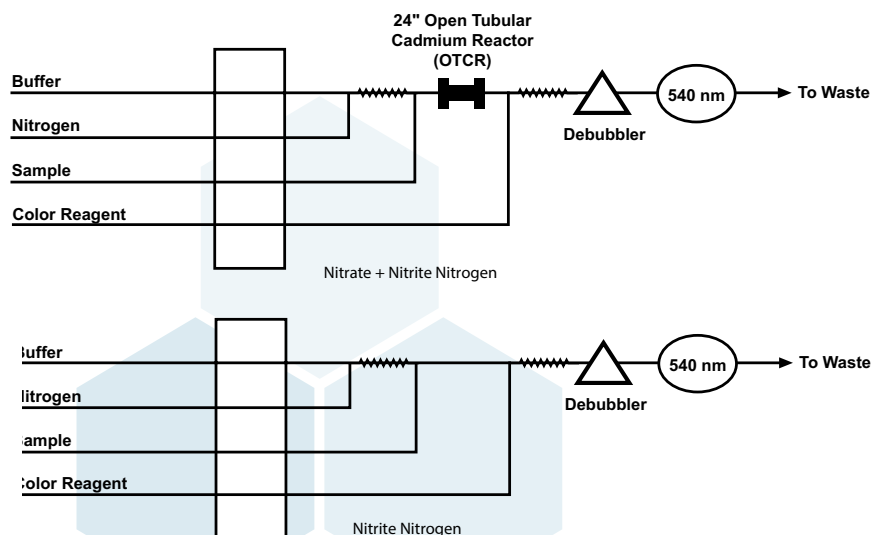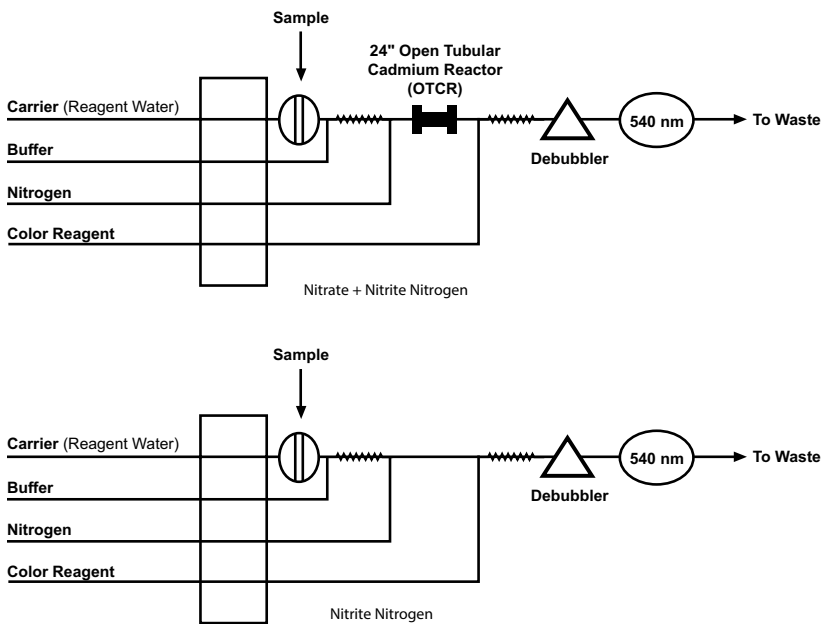
Figure 2. General FIA Flow Diagram for Nitrate plus Nitrite Nitrogen and Nitrite Nitrogen by USEPA 353.2

Reagents and Calibrants

Chemical Name	CAS #	Chemical Formula	Part Number
Ammonium chloride	12125-02-9	NH_4Cl	
Ammonium hydroxide	1336-21-6	NH_4OH	
Brij®-35 (21% solution)	9002-92-0	$(C_2H_4O)_nC_{12}H_{26}O$	326126
Cupric sulfate pentahydrate	7758-99-8	$CuSO_4 \bullet 5H_2O$	
Ethylenediaminetetraacetic acid, disodium salt dihydrate (EDTA)	6381-92-6	$C_{10}H_{16}N_2Na_2O_8 \bullet 2H_2O$	
Hydrochloric acid	7647-01-0	HCl	
Imidazole	288-32-4	$C_3H_4N_2$	
N-(1-Naphthyl)ethylenediamine dihydrochloride	1465-25-4	$C_{12}H_{14}N_2 \bullet 2HCl$	
Phosphoric acid	7664-38-2	H_3PO_4	
Potassium nitrate	7757-79-1	KNO_3	
Potassium nitrite	7758-09-0	KNO_2	
Sulfanilamide	63-74-1	$C_6H_8N_2O_2S$	
Water, deionized		H_2O	
Additionally, the following chemicals may be needed for sample preservation or treatment			
Chloroform	67-66-3	$CHCl_3$	

Summary of USEPA Method 353.2[1]

Method

- A filtered sample is passed through a column to quantitatively reduce nitrate to nitrite using cadmium metal. Nydahl provides a good discussion of nitrate reduction by cadmium metal.[4] The nitrite (that was originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and subsequently coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye that is measured colorimetrically at 540 nm.[2]
- Measure nitrite singly by performing the same analysis, but without the cadmium reduction coil. Nitrate is not reduced to nitrite without cadmium and is not detected because only nitrite forms the azo dye.
- The value for nitrate may be calculated by subtracting the nitrite value from the combined nitrate plus nitrite value.

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.
  NOTE: The alternative imidazole buffer solution is particularly adept at eliminating these interferences, and should be utilized whenever possible.
- 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 pH 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.
- Degas all reagents prior to analysis. 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.
- Chlorine may reduce the reduction efficiency of the cadmium reactor. Samples that may contain residual chlorine should be tested for reduction efficiency. When necessary, dechlorinate samples with sodium thiosulfate ($Na_2S_2O_3$).
- Norwitz and Keliher, as well as Nydahl have compiled a comprehensive study of interferences in the spectrophotometric analysis of nitrite.[4,5,6]
- Other compatible procedures for removing or suppressing interferences may be used, provided they do not adversely affect overall method performance.
- 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.

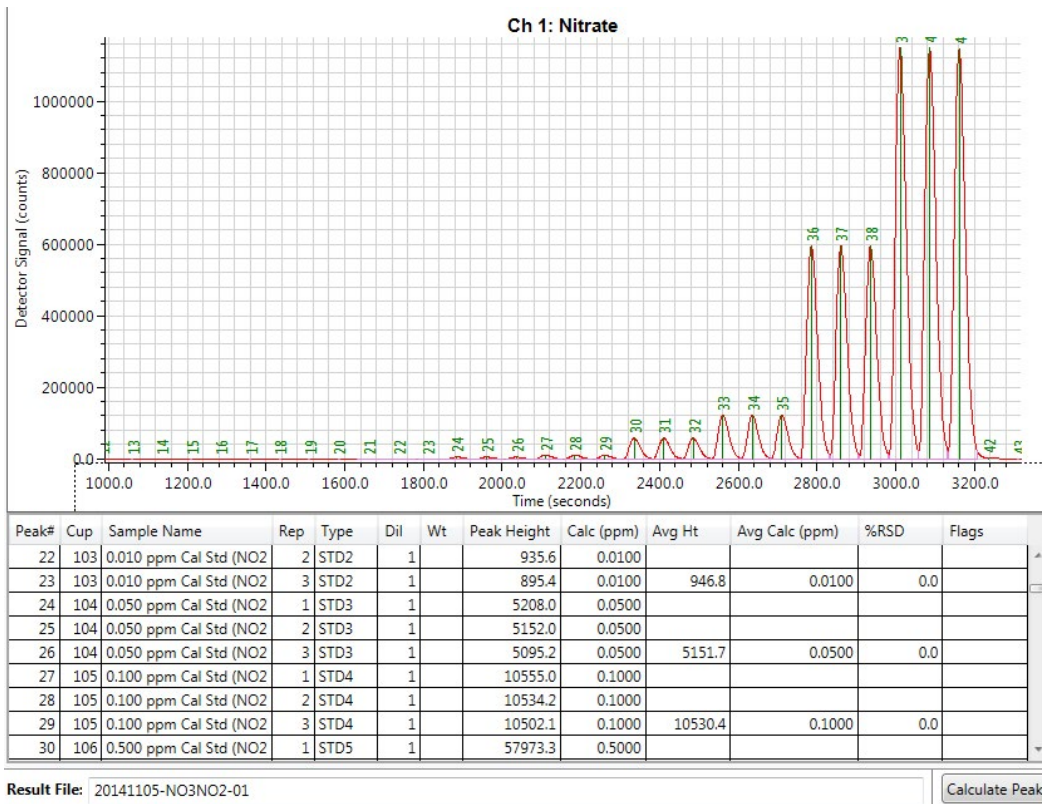Figure 3. Nitrate Plus Nitrite Calibration Series (SFA)

Peak#	Cup	Sample Name	Rep	Type	Dil	Wt	Peak Height	Calc (ppm)	Avg Ht	Avg Calc (ppm)	%RSD	Flags
22	103	0.010 ppm Cal Std (NO2	2	STD2	1		935.6	0.0100				
23	103	0.010 ppm Cal Std (NO2	3	STD2	1		895.4	0.0100	946.8	0.0100	0.0	
24	104	0.050 ppm Cal Std (NO2	1	STD3	1		5208.0	0.0500				
25	104	0.050 ppm Cal Std (NO2	2	STD3	1		5152.0	0.0500				
26	104	0.050 ppm Cal Std (NO2	3	STD3	1		5095.2	0.0500	5151.7	0.0500	0.0	
27	105	0.100 ppm Cal Std (NO2	1	STD4	1		10555.0	0.1000				
28	105	0.100 ppm Cal Std (NO2	2	STD4	1		10534.2	0.1000				
29	105	0.100 ppm Cal Std (NO2	3	STD4	1		10502.1	0.1000	10530.4	0.1000	0.0	
30	106	0.500 ppm Cal Std (NO2	1	STD5	1		57973.3	0.5000				

Result File: 20141105-NO3NO2-01

Calculate Peaks

Figure 4. Calibration Curve and Statistics (SFA)

Peak#	Cup	Sample Name	Rep	Type	Dil	Wt	Peak Height	Calc (ppm)	Avg Ht	Avg Calc (ppm)	%RSD	Flags
65	113	NO2 0.100 ppm	2	SPL	1		11306.1	0.1055				
66	113	NO2 0.100 ppm	3	SPL	1		11233.4	0.1048				
67	113	NO2 0.100 ppm	4	SPL	1		11207.3	0.1046				
68	113	NO2 0.100 ppm	5	SPL	1		11116.3	0.1039				
69	113	NO2 0.100 ppm	6	SPL	1		11071.4	0.1035				
70	113	NO2 0.100 ppm	7	SPL	1		10902.2	0.1021				
71	113	NO2 0.100 ppm	8	SPL	1		10824.7	0.1014				
72	113	NO2 0.100 ppm	9	SPL	1		10737.9	0.1007				
73	113	NO2 0.100 ppm	10	SPL	1		10536.2	0.0990	11027.7	0.1031	2.2	

Result File: 20141105-NO3NO2-01
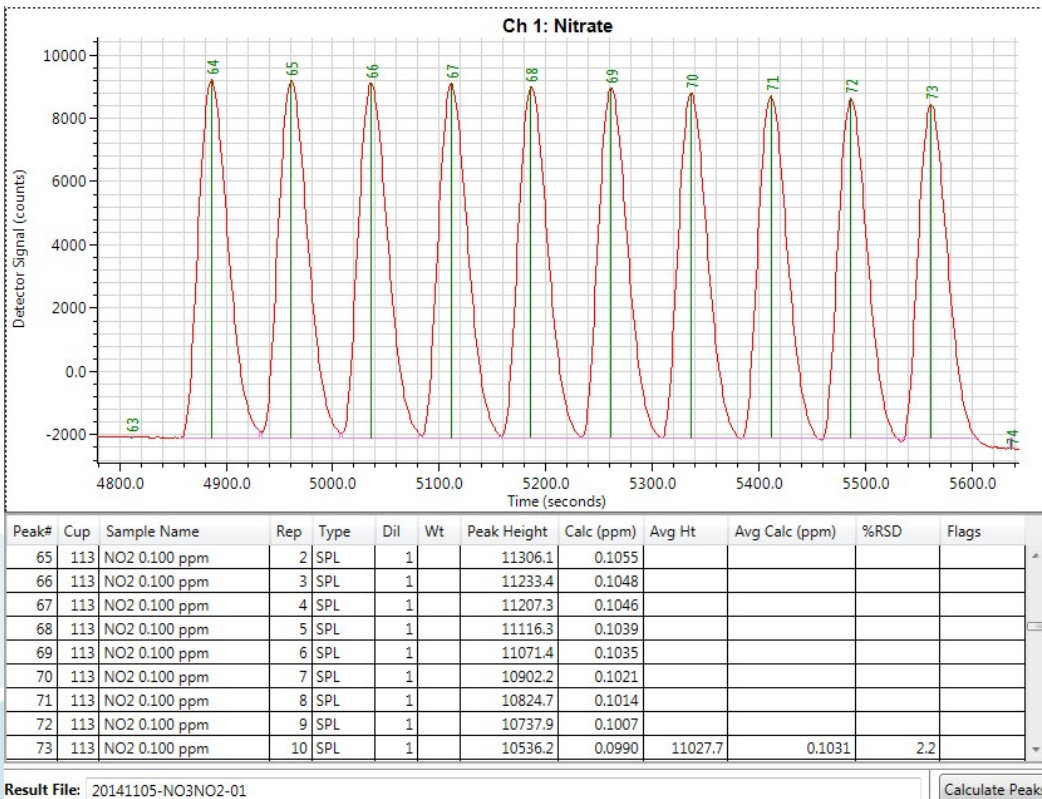
Calculate Peaks

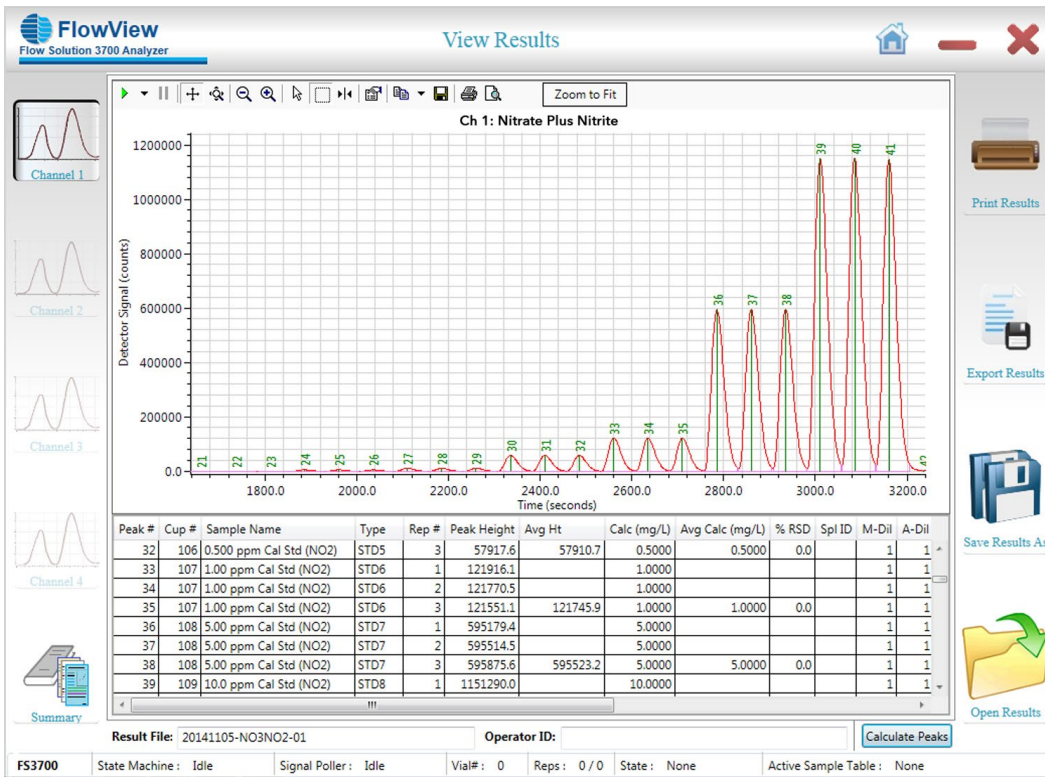Figure 5. Nitrate Plus Nitrite Calibration Series (FIA)

Figure 6. Calibration Curve and Statistics (FIA)

Figure 7. Nitrate Plus Nitrite Calibration Series (FIA)

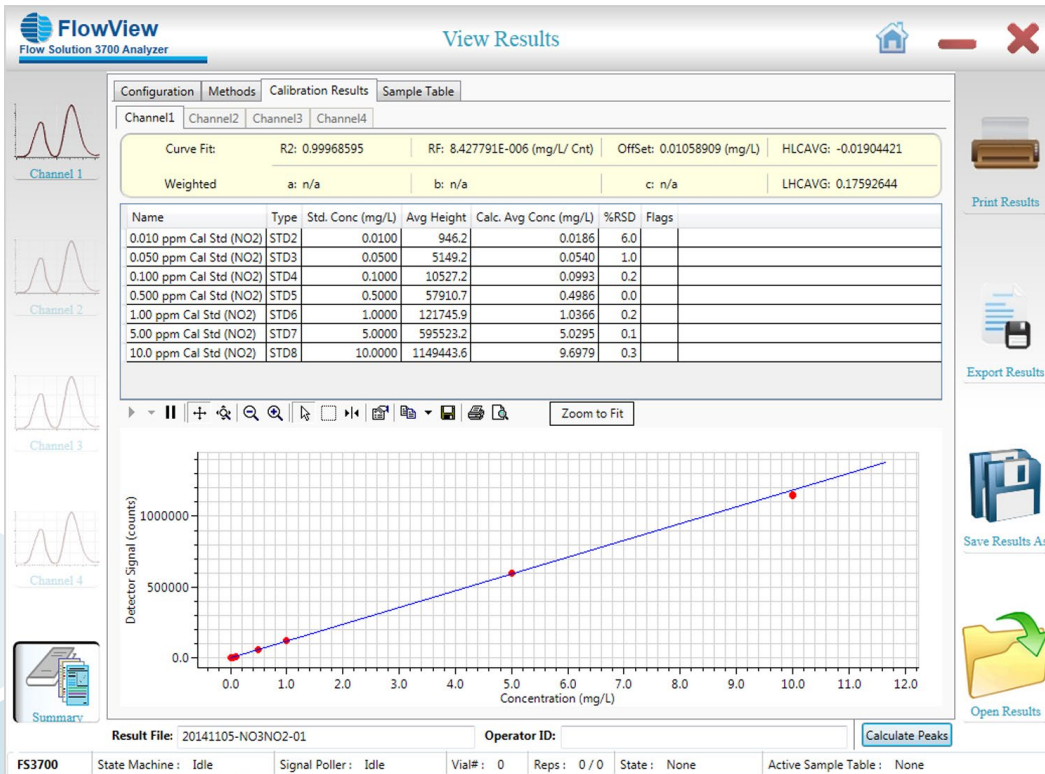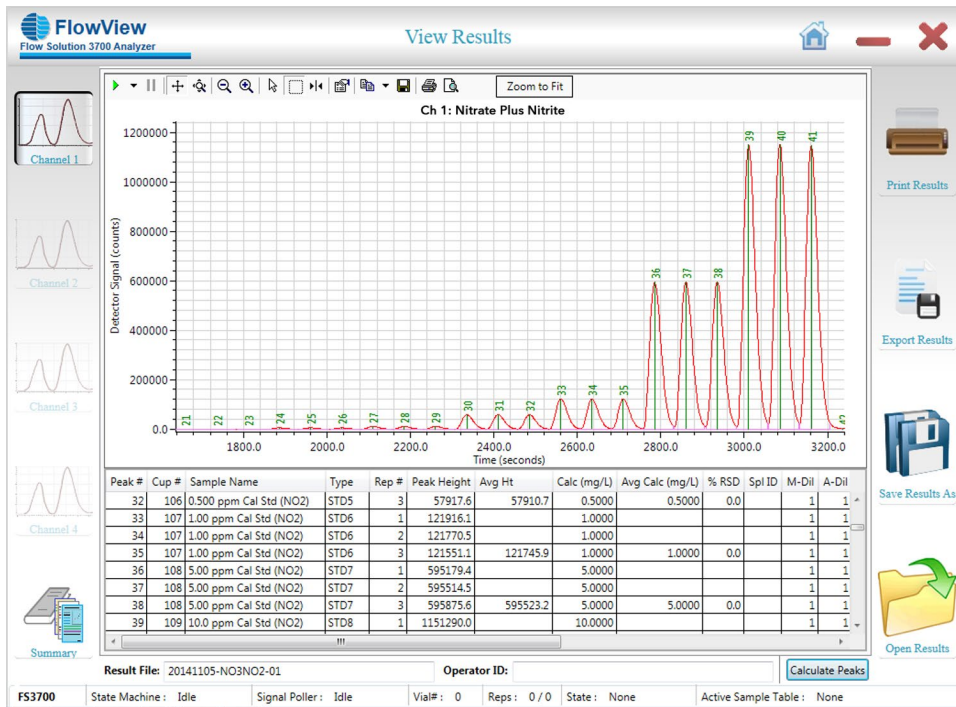Figure 8. Calibration Curve and Statistics (FIA)