

A Comparison of Two Ion Chromatography Analytical Columns for the Determination of Chloride, Nitrate, and Sulfate in Precipitation Samples

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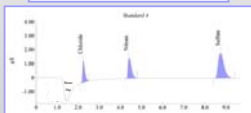


ABSTRACT

The Dionex AS4A column has been used for analysis of chloride, nitrate and sulfate in NADP National Trends Network (NTN) precipitation samples since 1986. This column uses a carbonate/bicarbonate methyl or ethyl phase. Manufacturers have reported improved capabilities with hydroxide eluent columns, such as the Dionex AS15. The AS4A and the AS15 were tested to determine whether their detection limits, column limits for the NADP NTN, FR25 and FR75 solutions (externally prepared quality control solutions targeting the 250 and 750 percent concentrations of all NTN samples), and separation performance are comparable. The AS15 will also be evaluated to see whether it can use improved and expanded NADP NTN ion chromatography capabilities for other analytes of interest. The AS15 column information shows that chlorate separation will be improved and that acetate, formate, and sulfite can be included with the common anions (chloride, nitrate, and sulfate) in a single run. Additionally, organic cations can be used with this column which would allow samples containing organic preservatives to be analyzed. Comparison data will be presented along with sample chromatograms.

AS4A Column AS4A Method

IC: Dionex DSX-500
Eluent: 1.75 mM NaHCO₃ / 1.80 mM Na₂CO₃
Detection: Suppressed Conductivity
Flow Rate: 2.0 mL/minute
Injection Volume: 250 µL
Run Time: 9.5 minutes (approximate)
Standards: Nitrate and Sulfate = 0.050 to 0.050 ppm
Chloride = 0.025 to 1.50 ppm

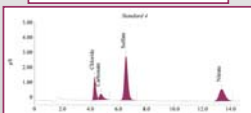


AS4A Column Chromatograms

The water dip and/or nitrate (data after chlorate) could interfere with chloride integration. In these cases baseline and/or peak markers would need to be manually adjusted.

AS15 Column Isocratic Method

IC: Dionex DSX-500
Eluent: 38 mM NaOH
Detection: Suppressed Conductivity
Flow Rate: 2.0 mL/minute
Injection Volume: 250 µL
Run Time: 14 minutes (approximate)
Standards: Nitrate and Sulfate = 0.050 to 0.050 ppm
Chloride = 0.025 to 1.50 ppm

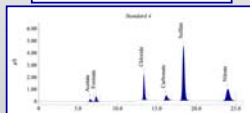


AS15 Column Chromatograms (Isocratic and Gradient Method)

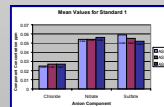
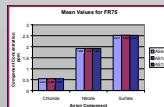
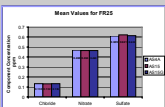
- The eluent needs to be prepared in small batches because carbon dioxide easily dissolves in sodium hydroxide eluent forming carbonate. Carbonate is a contaminant that results in a contamination peak that can affect anion retention times during analysis.
- The carbonate peak is very close to the chloride peak in the isocratic method and may interfere with chloride integration; manual adjustments would have to be made.
- Both methods require an additional column to acquire contaminants (ATC3 Column).
- The column manufacturer recommends a clean up procedure after each column use to remove contaminants, such as, carbonate from the ATC3 column. This procedure takes about one hour.
- The analysis times for both methods are much longer than the AS4A analysis time.

AS15 Column Gradient Method

IC: Dionex DSX-500
Eluent: 10 mM NaOH from 0 to 9.5 minutes
40 mM NaOH from 9.6 to 25.5 minutes
Detection: Suppressed Conductivity
Flow Rate: 1 mL/minute
Injection Volume: 250 µL
Run Time: 25.5 minutes (approximate)
Standards: Nitrate and Sulfate = 0.050 to 0.050 ppm
Chloride = 0.025 to 1.50 ppm
Acetate and Formate: 0.025 to 0.40 ppm



COMPARISON DATA



	Chloride		Nitrate		Sulfate	
	AS4A	AS15	AS4A	AS15	AS4A	AS15
Min.	0.10	0.10	0.05	0.05	0.05	0.05
Max.	1.00	1.00	1.00	1.00	1.00	1.00
Min. Det.	0.01	0.01	0.01	0.01	0.01	0.01
Max. Det.	0.1	0.1	0.1	0.1	0.1	0.1

	Chloride		Nitrate		Sulfate	
	AS4A	AS15	AS4A	AS15	AS4A	AS15
Min.	0.01	0.05	0.05	1.00	1.0	1.00
Max.	0.01	0.05	0.05	1.00	1.0	1.00
Min. Det.	0.01	0.05	0.01	0.01	0.01	0.01
Max. Det.	0.1	0.1	0.1	0.1	0.1	0.1

	Chloride		Nitrate		Sulfate	
	AS4A	AS15	AS4A	AS15	AS4A	AS15
Min.	0.01	0.05	0.05	0.05	0.05	0.05
Max.	0.01	0.05	0.05	0.05	0.05	0.05
Min. Det.	0.01	0.01	0.01	0.01	0.01	0.01
Max. Det.	0.1	0.1	0.1	0.1	0.1	0.1

CONCLUSION:

The chloride, nitrate, and sulfate standard deviations and MDAs for standard one are very close differing by less than 10 ppb when comparing the three methods for each anion. The chloride, nitrate, and sulfate FR25 and FR75 percent differences between the mean values for each anion are less than 2 percent when comparing all three methods for chloride, nitrate, and sulfate. All three methods compare well with each other. The correlation coefficients (R² values) for all anions and these methods were 0.999 or greater. The AS4A is the best column choice for the analysis of anions in NADP/NTN samples when considering ease of use, length of analysis, baseline noise, and the comparison data.

The gradient AS15 method is best suited for analyzing acetate and formate with chloride, nitrate, and sulfate for smaller sample sizes. Correlation Coefficients were greater than or equal to 0.999 for formate and approximately 0.996 for acetate. More work needs to be done to improve acetate analysis. An independent check sample needs to be formulated for these organic acids to verify these values. Other anions such as nitrite and sulfite, could be included in a single run.