

Equivalency Evaluation of Two Ion Chromatography Methods and Equipment

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Abstract: The National Atmospheric Deposition Program/Central Analytical Laboratory (NADP/CAL) uses two DX-500 Dionex Ion Chromatographs, purchased in 1995, for analysis of sulfate, nitrate, and chloride in precipitation samples. The current equipment utilizes a sodium bicarbonate/sodium carbonate (NaHCO₃/Na₂CO₃) eluent, AS4A columns, and a 250 µL sample loop. Two new Dionex ICS-2000s were purchased in June 2004. A potassium hydroxide (KOH) method and AS18 columns were used with the new equipment. Advantages of the new equipment include a smaller sample loop (25 µL), automated Eluent Generation, and heated column compartments. Both instruments use conductivity detection and AutoSuppression technology. Before using the KOH method and the new equipment for NADP sample analysis, a comparative study must be done. A side-by-side comparison was conducted to evaluate the differences and to minimize a step-function change in the data reported. NADP/CAL Quality Control samples and External Quality Assurance samples were analyzed to determine comparability. Preliminary data along with statistical analysis are presented.

AS4A Column Isocratic Method

IC: Dionex DX-500
Eluent: 1.75 mM NaHCO₃/1.80 mM Na₂CO₃
Column: Dionex AG4A/AS4A
Detection: Suppressed Conductivity
Flow Rate: 2.0 mL/minute
Injection Volume: 250 µL
Suppressor: Dionex ASRS Ultra-2
Autosuppression Technology
Run time: 9.5 minutes (approximate)
Standards: Nitrate and Sulfate = 0.050 to 6.00 ppm
Chloride = 0.025 to 1.50 ppm

AS18 Column Isocratic Method

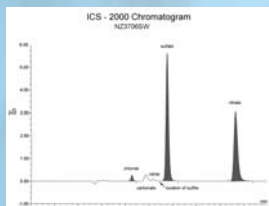
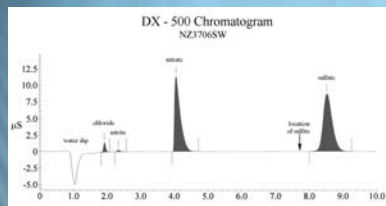
IC: Dionex ICS-2000
Eluent: 35 mM KOH
Column: Dionex AG18/AS18
Detection: Suppressed Conductivity
Flow Rate: 1.0 mL/minute
Injection Volume: 25 µL
Suppressor: Dionex ASRS Ultra-2
Autosuppression Technology
Run time: 9.5 minutes (approximate)
Standards: Nitrate and Sulfate = 0.050 to 6.00 ppm
Chloride = 0.025 to 1.50 ppm

Purchased 1995
Over 90,000 analyses completed



DX-500 vs. ICS-2000

Purchased 2004



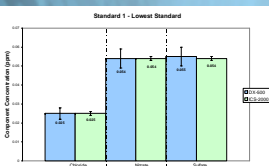
Disadvantages of DX-500

- Eluent must be prepared by analyst
- No in-line degassing
- Unheated column compartments
- The water dip and/or nitrate peak (elutes after chloride) could interfere with chloride integration. In these cases baselines or peak markers would need to be manually adjusted.

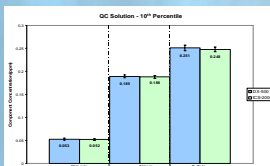
Advantages of ICS-2000

- Eluent Generation – eliminates need to manually prepare eluent
- In-line degassing – produces more stable baselines
- Heated column compartments – provide more stable IC systems (IC systems are temperature dependent)
- No peak interferences from water dip
- Increased Sensitivity – with reduced injection volume

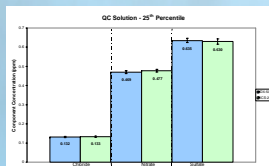
NADP/CAL Quality Control Samples Comparison



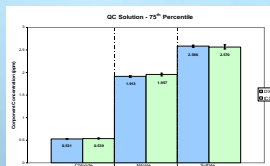
	Chloride (ppm)		Nitrate (ppm)		Sulfate (ppm)	
	DX-500	ICS-2000	DX-500	ICS-2000	DX-500	ICS-2000
Target	0.025	0.025	0.050	0.050	0.050	0.050
Min.	0.016	0.022	0.039	0.051	0.040	0.051
Mean	0.025	0.025	0.054	0.054	0.055	0.054
Max.	0.034	0.028	0.069	0.067	0.070	0.067
SD	0.003	0.001	0.006	0.001	0.006	0.001
RSD (%)	12.00	4.00	9.26	1.85	9.09	1.85
n	20	15	20	15	20	15



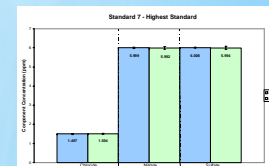
	Chloride (ppm)		Nitrate (ppm)		Sulfate (ppm)	
	DX-500	ICS-2000	DX-500	ICS-2000	DX-500	ICS-2000
Min.	0.047	0.046	0.180	0.179	0.233	0.233
Mean	0.053	0.052	0.189	0.188	0.251	0.248
Max.	0.069	0.058	0.198	0.197	0.269	0.263
SD	0.002	0.002	0.003	0.003	0.006	0.005
RSD (%)	3.77	3.85	1.59	1.60	2.39	2.02
n	22	15	22	15	22	15



	Chloride (ppm)		Nitrate (ppm)		Sulfate (ppm)	
	DX-500	ICS-2000	DX-500	ICS-2000	DX-500	ICS-2000
Min.	0.123	0.124	0.468	0.450	0.602	0.588
Mean	0.132	0.133	0.469	0.477	0.635	0.630
Max.	0.141	0.142	0.490	0.498	0.669	0.672
SD	0.003	0.003	0.007	0.007	0.011	0.014
RSD (%)	2.27	2.26	1.49	1.47	1.73	2.22
n	24	15	24	15	24	15



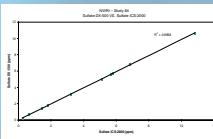
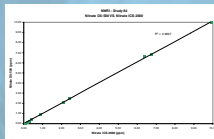
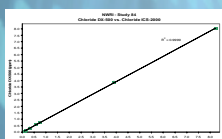
	Chloride (ppm)		Nitrate (ppm)		Sulfate (ppm)	
	DX-500	ICS-2000	DX-500	ICS-2000	DX-500	ICS-2000
Min.	0.516	0.515	1.82	1.873	2.514	2.432
Mean	0.531	0.539	1.913	1.937	2.586	2.570
Max.	0.548	0.550	1.964	2.041	2.658	2.709
SD	0.009	0.009	0.017	0.028	0.024	0.046
RSD (%)	0.94	1.48	0.89	1.43	0.93	1.79
n	24	15	24	15	24	15



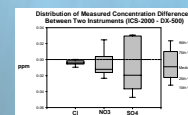
	Chloride (ppm)		Nitrate (ppm)		Sulfate (ppm)	
	DX-500	ICS-2000	DX-500	ICS-2000	DX-500	ICS-2000
Target	1.500	1.500	4.000	4.000	6.000	6.000
Min.	1.487	1.438	3.993	3.778	5.920	5.745
Mean	1.487	1.504	3.999	3.995	6.008	5.934
Max.	1.527	1.570	4.095	4.161	6.086	6.243
SD	0.019	0.022	0.032	0.062	0.026	0.063
RSD (%)	0.91	0.91	0.81	0.91	0.90	0.91
n	20	15	20	15	20	15

National Water Research Institute (NWRI) Natural Rain and Soft Waters Study - #84 Comparison

NWRI Study #84 samples were analyzed on the same day on the DX-500 and the ICS-2000. One-to-one graphs were constructed. The y-axis = DX-500 data and the x-axis = ICS-2000 data.



National Atmospheric Deposition Program/National Trends Network Comparison



Paired t-test Results:
 Chloride: t = -0.017, -0.811, -0.735
 P = 0.918, 0.444, 0.468
 df = 7, 7, 7
 * Indicates a statistically significant difference for chloride between the two instruments. The n was small for the data set. Most pairs of NADP/NTN samples will be analyzed in the future. This will result in a larger data set to determine a significant difference.

NWRI #	Chloride (ppm) DX500	Chloride (ppm) ICS-2000	NWRI Median*
1	0.110	0.102	0.11
2	0.111	0.109	0.12
3	0.092	0.088	0.09
4	0.126	0.121	0.13
5	0.769	0.743	0.74
6	0.307	0.303	0.30
7	0.317	0.308	0.31
8	3.904	3.880	3.9
9	0.691	0.683	0.68
10	8.225	8.015	8.1

*Median for all participating labs - n=30

NWRI #	Nitrate (ppm) DX500	Nitrate (ppm) ICS-2000	NWRI Median*
1	0.096	0.079	0.084
2	2.401	2.444	2.39
3	0.861	0.877	0.872
4	2.099	2.103	2.09
5	0.268	0.256	0.266
6	6.403	6.653	6.6
7	6.740	6.804	6.77
8	0.411	0.394	0.403
9	8.900	8.971	8.97
10	0.188	0.163	0.181

*Median for all participating labs - n=30

NWRI #	Sulfate (ppm) DX500	Sulfate (ppm) ICS-2000	NWRI Median*
1	0.247	0.220	0.26
2	1.813	1.835	1.83
3	0.669	0.660	0.66
4	1.462	1.460	1.49
5	6.832	6.873	7.0
6	5.217	5.176	5.2
7	5.120	5.025	5.1
8	5.786	5.680	5.8
9	6.697	6.560	6.7
10	10.815	10.659	10.8

*Median for all participating labs - n=30

Sample #	Chloride (ppm)			Nitrate (ppm)			Sulfate (ppm)		
	ICS-2000	DX-500	% Diff (C)	ICS-2000	DX-500	% Diff (N ₂)	ICS-2000	DX-500	% Diff (SO ₄ ²⁻)
NZ015SW	0.049	0.050	-2.0	0.461	0.473	-2.5	0.331	0.361	-8.3
NZ020SW	0.172	0.171	0.6	2.227	2.195	1.5	3.918	3.769	0.8
NZ025SW	0.031	0.035	-13.9	1.950	1.942	0.5	1.445	1.455	-0.7
NZ035SW	0.212	0.217	-2.3	0.642	0.668	-3.9	0.673	0.716	-6.0
NZ125SW	0.018	0.020	-10.0	0.540	0.557	-3.1	0.341	0.370	-7.8
NZ195SW	0.080	0.083	-3.6	0.723	0.735	-1.6	2.138	2.107	1.5
NZ176SW	0.144	0.120	-8.0	3.860	3.965	-4.4	3.378	3.527	-4.4
NZ022SW	1.130	1.141	-1.0	1.940	1.940	0.0	2.593	2.563	1.2

Conclusion: Preliminary data comparing Dionex's DX-500 to Dionex's ICS-2000 is presented in this poster. The ICS-2000 instruments yielded better RSD values for the NADP/CAL Quality Control samples at the lower level and about the same at the 10th percentile level compared with the DX-500 instruments. The RSD values from all ion chromatographs were about the same at the 25th percentile level for chloride and nitrate, but not for sulfate. The sulfate RSD value at the 25th percentile and the 75th percentile levels were higher for the ICS-2000 than for the DX-500. The ICS-2000 displays better precision within the lower concentration levels and less precision within the higher levels.

The NWRI comparison data produced results with correlation coefficients greater than 0.999, indicating a high degree of similarity between the two data sets.

Eight NADP/NTN samples were analyzed on the same day and all the data points exhibit less than a 10% difference from one another, except one chloride pair that was 13.9%. The chloride values associated with the 13.9% difference only differ by 5 ppb and are below 10 times the MDL. A 20% difference is acceptable at this level according to the CAL Quality Assurance Plan.

This study will continue into the future with a comparison of hundreds of natural rain samples collected by the CAL. These samples will be run side-by-side on both systems to eliminate any chemical variations that may have occurred in the samples over time. The results of that study will be presented at a future meeting.