Optimization and Preparation of Precipitation Analyses

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The Central Analytical Laboratory (CAL), located at the Illinois State Water Survey, receives approximately 240 samples per week from the National Atmospheric Deposition Program (NADP)/National Trends Network (NTN) and the NADP/Atmospheric Integrated Research Monitoring Network (AIRMoN). Precipitation samples are collected from sites in the United States, Puerto Rico, and the Virgin Islands. The precipitation samples are analyzed by ion chromatography for trace level concentrations of nitrate, sulfate, and chloride. Networks of this size and importance require careful and accurate laboratory analyses.

Two DX-500 ion chromatographs with conductivity detection are used to analyze these samples. The method detection limits are: 0.004 ppm for chloride and 0.008 ppm for nitrate and sulfate. The upper standard concentrations are: 1.500 ppm for chloride and 6.000 ppm for nitrate and sulfate.

To achieve the results required by the NADP, it is essential to optimize ion chromatographic operating conditions, implement stringent sample preparation procedures, and maintain quality assurance practices. This poster will present the methods and procedures used to obtain and maintain high quality results.

mple Collection and Preparation

le Procedures:

and check each shipment of collection vessels ags, buckets, and bottles). Document any mination.

tor collection vessels used and reused in the rk.

ean sample vials to eliminate contamination. leionized water that is 17.5 megohms/cm or er for all reagents and standards.

d contamination from direct hand contact with les, standards, sample containers, and vials. lish a work zone for pouring samples and ring dilutions.

iltration or refrigeration to slow down the dation of samples.

k and monitor all filters used for sample rvation for contamination.


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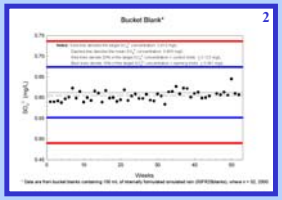

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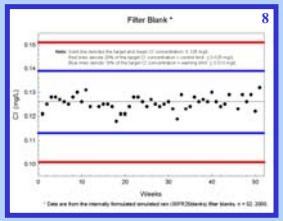

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Equipment Optimization, Preparation, and Monitoring

These procedures are used to achieve and maintain high quality results and proper equipment operation:

9 * Filter all samples to avoid plugging sample lines and extend life of precolumn.

10 * Use a 250 μL loop for lower detection limits.

11 * Start each run with calibration standards, and include a second set of standards in the run to be used if recalibration is necessary.

12 * Use a quadratic curve fit and area counts under the curve to calculate concentration values requiring correlation coefficients of ≥ 0.999 (r^2 values).

13 * Establish Method Detection Limits (MDLs), confirm periodically, and reestablish yearly. (Fed. Reg., Vol. 49. No. 209, App. B to Part 136)

* Purchase primary standards yearly. Analyze against old primary standards and an external standard or quality control solution.
* Make secondary standards every two weeks.
* Monitor equipment for correct operation.
* Monitor and document eluent and system pressure to help isolate problems when and if they occur.
* Expedite large sample throughput with use of a Laboratory Information Management System (LIMS).

Schedule maintenance and replacement of consumables:

* Schedule column, suppressor, and tubing replacement to avoid problems before they happen.
* Replace anion guard column at least every six months.
* Replace analytical column and anion suppressor at least every year.
* Replace sample tubing yearly and other tubing and consumables as needed.
* Keep manufacturers recommended maintenance schedules (i.e. pump maintenance and cell calibration).


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Example Schedule

Line	Sample Type		Line	Sample Type		Line	Sample Type	
1	autocal1		22	Standard 1		44	NV41585W	
2	autocal2		23	FR25120100	QCS	45	NV42303W	
3	autocal3	1st set of Calibration Standards	24	NV41858W		46	NV42015W	
4	autocal4		25	NV41925W		47	NV42023W	
5	autocal5		26	NV41935W		48	NV42029W	
6	autocal6		27	NV41945W		49	FR25120109	QCS
7	BK		28	NV41955W		50	S1	
8	FR25120100	QCS	29	NV41965W		51	S2	2nd set of Standards
9	FR25120100		30	NV41975W		52	S3	
10	NV41935W		31	NV41985W		53	S4	
11	NV41935W		32	NV41995W		54	S5	
12	NV41715W		33	NV41905W		55	S6	
13	NV41725W		34	NV41915W		56	FR25120100	QCS
14	NV41735W		35	NV41925W		57	FR25120100	QCS
15	NV41745W		36	NV41935W		58	Standard 6	
16	NV41755W		37	FR25120100	QCS	59	NV42005W	
17	NV41765W		38	NV41955W		60	NV42015W	
18	NV41775W		39	NV41945W		61	NV42073W	
19	NV41785W		40	NV41955W		62	NV42083W	
20	NV41795W		41	NV41965W		63	NV42093W	
21	NV41805W		42	NV41975W		64	NV42103W	
			43	NV41985W		65	NV42115W	

Line	Sample Type	
65	NV42125W	
67	NV42135W	
68	NV42145W	
69	NV42155W	
70	Standard 1	
71	FR25120100	QCS
72	NV42165W	
73	NV42175W	
74	NV42185W	
75	NV42195W	
76	NV42205W	
77	NV42215W	
78	NV42225W	
79	NV42235W	
80	NV42245W	
81	NV42255W	
82	NV42265W	
83	Sample	
84	Standard 6	
85	FR25120100	QCS
86	FR25120100	
87	B	

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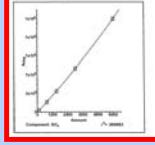
Example Calibration Curve with r^2 Values



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METHOD DETECTION LIMITS (MDL) FOR THE ION CHROMATOGRAPH

Ion	Mean	Median	Standard Deviation	Method Detection Limit (MDL)	Minimum	Minimum	n
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	
Cl	0.053	0.054	0.0016	0.004	0.056	0.049	26
NO_3	0.190	0.189	0.0029	0.008	0.196	0.180	26
SO_4	0.250	0.250	0.0032	0.008	0.257	0.242	26

Notes:
The solution used was an internally formulated simulated rain (SSFR2010).
The student's t value used for the 99% percent confidence level and 25 degrees of freedom was 2.485.
The solutions was unfiltered internal blind samples analyzed over 12 months.

Quality Control

The Central Analytical Laboratory (CAL) has a multilevel program that includes Analyst, Lab Management, and External Quality Control (QC). Analyst QC will be covered in this Poster.

Analysts Quality Control

14 * Check all chromatograms for proper peak shape and separation.

15 * Repeat samples with problem chromatograms.

11 * Analyze Quality Control Standard (QCS) solutions and the highest and lowest standards at least every 12 samples.

16 * Monitor system trends over time using control charts in order to take corrective actions before warning limits are exceeded.

17 * Compare diluted concentrations with undiluted concentrations.

* Reanalyze samples if values do not meet network standards and establish a random reanalysis system.
* Analyze a DI blank after each set of calibration standards to monitor the DI water and system contamination.

Corrective actions:

* Reanalyze the first QCS after the calibration standards, if they are out of control.
* Recalibrate instrument, if first QCS solutions are still out of control.
* Isolate problem and correct, then recalibrate, if first QCS solutions continue to be out of control.
* Reanalyze the corresponding samples, if QCS solutions are out of control during analyses and recalibration does not help.

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Dilution Accuracy

Sample ID NV3741SW

Ion	Undiluted Concentrations	Diluted Concentrations
Cl^-	0.332	0.335
NO_3^-	4.826	4.806
SO_4^{-2}	9.293	10.085

Note: The undiluted SO_4^{-2} concentration was above the highest SO_4^{-2} standard 6.00 ppm. The sample was diluted 1:4. The Cl and NO_3^- concentrations are compared as a check of the dilution. The SO_4^{-2} values are quite different and show that extrapolating this quadratic curve will give you lower values than using values from a diluted sample that is in your standard working range.