2019 Research Triangle Institute Quality Assurance Report

Introduction

Within 60 days of sample receipt, filters are extracted, and then IC is used to analyze for Cl^-, $NO2^-$, $NO3^-$, and $SO4^{2-}$, following the NPS–approved RTI Anion Cation Analysis by Ion Chromatography (IC) SOP. The collected data are reduced, and then submitted to the IMPROVE Operations Contractor (OC). Instruments are calibrated daily by using standards prepared by serial dilutions of stock standards traceable to NIST. Analyte calibration ranges are extended to cover typical concentrations measured for ambient air samples. Chloride is calibrated from 0.010 ppm to 2.0 ppm, $NO2^-$, $NO3^-$, and $SO4^{2-}$ are calibrated from 0.050 ppm to 10.0 ppm. The correlation coefficient is verified to be 0.999 or greater for every calibration. Minimum Detection Limits shown in Table 1 are used as reference points for qualifying duplicate and reanalysis precision. Network detection limits for ions are calculated by University of California at Davis staff when data are received from Research Triangle Institute (RTI).

Minimum Detection Limits (MDL's)

Table 1. MDL's

	Chloride	Nitrite	Nitrate	Sulfate
MDL	0.005 ppm	0.010 ppm	0.008 ppm	0.011 ppm

After ion chromatograph calibration, an analytical sequence consisting of 50 field samples, extraction QC checks, three sets of replicate injection samples, two matrix spikes, and continuing calibration verification (CCV) standards are queued for analysis.

CCV QC Standards

The CCV QC standards are analyzed immediately following the calibration, at the end of the sequence, and after every set of 10 field samples. The CCV QC standards are prepared at concentrations that confirm instrument performance and calibration stability at the low, middle, mid-high, and high calibration ranges. Recoveries are determined by dividing the measured concentration by the target concentration. Measured concentrations must be ± 10% of nominal values. CCV QC solutions bracket 10 samples analyzed, if a CCV QC fails and there are no other CCV QC samples analyzed before or after the

bracketed set of 10 samples, all samples within this bracket are reanalyzed. CCV QC recoveries are shown in Table 2 for all ions.

Table 2. QC CCV recoveries

Chloride	Low	Mid	Mid-High	High
Median recovery	101%	101%	101%	102%
Average recovery	101%	101%	100%	102%
Maximum recovery	249%	107%	104%	106%
Minimum recovery	26.0%	95.0%	1.88%	97.6%
Failures	0.39 %	0%	0.97%	0%
Count	770	1190	723	400
Nitrite				
Median recovery	97.1%	98.1%	100%	101%
Average recovery	97.3%	98.2%	99.1%	101%
Maximum recovery	245%	107%	107%	107%
Minimum recovery	23.8%	91.0%	1.47%	96.0%
Failures	0.39%	0%	0.97%	0%
Count	770	1190	723	400
Nitrate				
Median recovery	98.7%	98.5%	99.8%	99.8%
Average recovery	98.8%	98.3%	98.8%	99.3%
Maximum recovery	244%	104%	102%	102%
Minimum recovery	27.3%	90.5%	1.96%	93.7%
Failures	0.39%	0%	0.41%	0%
Count	770	1190	723	400
Sulfate				
Median recovery	98.3%	99.4%	99.7%	100%
Average recovery	99.3%	99.3%	98.7%	100%
Maximum recovery	247%	104%	102%	103%
Minimum recovery	26.4%	94.6%	1.98%	96.9%
Failures	0.39 %	0.07%	0.41%	0%
Count	770	1190	723	400

Replicate Samples

Replicate samples are a sample extract poured twice and measured sequentially in the analytical batch. They are used to by the IMPROVE OC to calculate analytical precision. All analytical batches include 3 sets of replicate samples and 50 National Park Service samples. The relative percent difference for replicate samples calculated by the difference divided by the average must be ± 10% when sample concentrations are greater than ten times the stated MDL and ± 100% when sample concentrations are at the MDL and up to ten times the stated MDL. Table 3 shows results for all replicate samples. Failures are repeated, if all other QC samples pass, only the duplicate samples are repeated. If there is more than one failure the entire batch is reanalyzed.

Table 3. Replicate samples relative percent differences.

	Chloride	Nitrite	Nitrate	Sulfate
Median RPD	0.10%	0%	0.07%	0.05%
Average RPD	0.05%	6.79%	0.11%	0.25%
Max RPD	64.1%	200%	40.1%	200%
Min RPD	-130%	-200%	-37.7%	-146%
Count	1002	1002	1002	1002
Percentage of Failures	0.30%	0%	0.10%	0.20%

Matrix Spikes

Samples are spiked at a rate of 2 spikes per batch of 50 samples. The spike recoveries are acceptable from 90% - 110%. Table 4 lists spike recoveries for all ions. Samples are repeated when spike recoveries fail and the reason for failure is unknown. If failure occurs due to the wrong spiking formula, they are not repeated.

Table 4. Spike recoveries.

	Chloride	Nitrite	Nitrate	Sulfate
Median Recovery	101%	99.5%	101%	101%
Average Recovery	101%	99.6%	101%	101%
Max Recovery	111%	109%	113%	112%
Min Recovery	82.3%	80.0%	83.5%	82.7%
Count	668	668	668	668
Percentage of Failures	0.45%	0.15%	0.60%	0.75%

Extraction QC Checks

Extraction QC checks are prepared during the extraction process to evaluate artifacts introduced throughout the extraction and analytical process. There are two types of extraction QC's: laboratory control spikes (LCS) and method blanks (MB). LCS extraction QC's are prepared by spiking an empty extraction vial with a concentrated stock solution and diluting with the same volume of deionized water (DI) used to extract NPS samples. The concentrations are targeted to match the low, middle, and high CCV QC standards used to verify the calibration of the IC systems. Method blanks are prepared by filling an empty extraction vial with DI using the same volume as is used for NPS samples. During the extraction of the NPS samples, filters are placed into the empty pre-labeled extraction vials and placed in a large test tube rack following the order listed on the chain of custody (COC) received from the OC. Extraction QC's are added to the list of samples on the COC beginning with 2 extraction QC's before the first sample on the COC. Additional extraction QC's are added at a rate of 1-2 following every 25 samples. The extraction QC's are prepared at the time that NPS samples are extracted and so the extraction QC's are interspersed between samples in the test tube racks prior to DI water being added. Results for method blanks are shown in Table 5. The results for the recoveries of the extraction QC checks are shown in Table 6.

Table 5. Concentrations measured in method blanks.

	Chloride	Nitrite	Nitrate	Sulfate
Median Concentration	0 ppm	0 ppm	0 ppm	0 ppm
Average Concentration	0.002 ppm	0.005 ppm	0.003 ppm	0.001 ppm
Maximum concentration	0.401 ppm	0.021 ppm	0.043 ppm	0.487ppm
Minimum Concentration	0 ppm	0 ppm	0 ppm	0 ppm
Count	578	578	578	578
Percentage of Samples with Measured Concentrations Exceeding MDL	5.4%	1.6%	0.7%	0.7%

Table 6. Extraction QC check recoveries.

Chloride	Low	Mid	High
Median recovery	101%	99.5%	100%
Average recovery	101%	99.6%	101%
Maximum recovery	106%	101%	104%
Minimum recovery	97.8%	97.1%	96.3%
Count	213	250	298
Percentage with Recovery Outside Acceptable Range	0%	0%	0%
Nitrite	**Low**	**Mid**	**High**
Median recovery	95.5%	101%	101%
Average recovery	95.5%	101%	101%
Maximum recovery	118%	106%	104%
Minimum recovery	90.7%	98.5%	96.8%
Count	213	250	298
Percentage with Recovery Outside Acceptable Range	0.47%	0%	0
Nitrate	**Low**	**Mid**	**High**
Median recovery	97.5%	101%	98.6%

Average recovery	97.4%	101%	98.5%
Maximum recovery	105%	102%	100%
Minimum recovery	92.6%	97.8%	95.7%
Count	213	250	298
Percentage with Recovery Outside Acceptable Range	0%	0%	0%
Sulfate	Low	Mid	High
Median recovery	97.8%	101%	99.5%
Average recovery	97.7%	101%	99.6%
Maximum recovery	101%	102%	104%
Minimum recovery	94.6%	98.9%	96.7%
Count	213	250	298
Percentage with Recovery Outside Acceptable Range	0	0	0

Sample Reanalysis

As another check of precision, 5% of all samples are reanalyzed using different instruments and different calibration curves. These samples are compared by calculating the relative percent difference as the difference over the average between the original and reanalyzed results. Table 7 lists results for all reanalyzed samples. Samples with measured concentrations at or up to 10 times the detection limit may be +/- 200%. Samples with measured concentrations at 10 times the detection limit up to 100 times the MDL must be within 20%.

Table 7. Relative Percent Differences Measured for Reanalyzed Samples.

	Chloride	Nitrite	Nitrate	Sulfate
Median RPD	1.04%	1.14%	0.44%	0.49%
Average RPD	1.59%	16.0%	0.63%	1.03%
Max RPD	90.7%	200%	200%	200%
Min RPD	-198%	-200%	-200%	-200%
% Failures	0.60%	0 %	0.26%	0.43%
Count	1165	1165	1165	1165

Extraction Efficiencies

Filters are routinely extracted a second time to measure extraction efficiencies. Table 8 lists the extraction efficiencies for all ions calculated by dividing the measured concentration in the second extract by the sum of the measured concentrations for both extracts. All extraction efficiencies meet those specified in the statement of work. Extraction efficiencies are not reported for nitrite, no results are reported for nitrite.

Table 8. Average Extraction Efficiencies

	Chloride	Nitrite	Nitrate	Sulfate
Average Extraction Efficiency	97.4%		97.5%	99.9%

Quality Assurance Standards

An additional third source QA standard prepared by an external vender and diluted is analyzed routinely to verify the accuracy of the IC systems. The standard is diluted three different ways to create QA samples with concentrations that mimic the 25th, 50th, and 75th percentile concentrations routinely measured in NPS samples. Tables 9, 10, & 11 shows target concentrations and RPD's for the 25th 50th and 75th percentile solutions.

Table 9. Target Concentrations and Relative Recovery for the 25th Percentile QA solution.

QA25	Chloride	Nitrite	Nitrate	Sulfate
Target Concentration	0.025 ppm	0.011 ppm	0.150 ppm	0.500 ppm
Average Measured Concentration	0.025 ppm	0.011 ppm	0.147 ppm	0.492 ppm
Average Recovery	102%	105%	96.2%	96.9%
Median Recovery	103%	103%	96.9%	97.8
Max Recovery	156%	950%	143%	120%
Min Recovery	68.7%	0%	73.6%	62.2%
Count	375	375	375	375

Table 10. Target Concentrations and Recovery for the 50th Percentile QA solution.

QA50	Chloride	Nitrite	Nitrate	Sulfate
Target Concentration	0.050 ppm	0.022 ppm	0.300 ppm	1.00 ppm
Average Measured Concentration	0.051 ppm	0.022 ppm	0.293 ppm	0.988ppm
Average Recovery	103%	93.5%	97.8%	97.9%
Median Recovery	102%	93.3%	97.9%	98.8%
Max Recovery	118%	134%	103%	103%
Min Recovery	95.7%	44.2%	93.1%	95.0%
Count	385	385	385	385

Table 11. Target Concentrations and Recovery for the 75th Percentile QA solution.

QA75	Chloride	Nitrite	Nitrate	Sulfate
Target Concentration	0.100 ppm	0.044 ppm	0.600 ppm	2.00 ppm
Average Measured Concentration	0.103 ppm	0.042 ppm	0.589 ppm	1.98ppm
Average Recovery	103%	94.5%	98.1%	99.0%
Median Recovery	103%	94.8%	98.1%	99.2%
Max Recovery	109%	107%	103%	102%
Min Recovery	98.1%	65.1%	94.5%	39.9%
Count	385	385	385	385

External PT Study

Throughout 2019, the ions laboratory participated in the National Atmospheric Deposition Program/Mercury Deposition Network Interlaboratory Comparison Program. The program is administered by the United States Geological Survey (USGS) Branch of Quality Systems. Four samples per month are sent to participating laboratories for analysis. The analytical precision of participating laboratories is calculated yearly, and results may be viewed via the following website.

https://bqs.usgs.gov/PCQA/Interlaboratory_Comparison/index.php