2017 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 (MDL's)

Table 1. MDL's

	Chloride	Nitrite	Nitrate	Sulfate
MDL	0.005 ppm	0.005 ppm	0.010 ppm	0.008 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	99.9%	99.8%	101%	99.5%
Average recovery	102%	100%	101%	99.5%
Maximum recovery	258%	107%	107%	105%
Minimum recovery	67.7%	94.2%	96.4%	95.0%
Failures	1.21%	0	0	0
Count	826	1355	647	442
Nitrite				
Median recovery	98.6%	99.4%	99.4%	98.8%
Average recovery	98.7%	99.7%	99.7%	99.2%
Maximum recovery	110%	127%	108%	109%
Minimum recovery	90.5%	91.7%	93.2%	92.3%
Failures	0	0.221%	0	0
Count	826	1355	647	442
Nitrate				
Median recovery	98.8%	99.2%	99.8%	99.8%
Average recovery	98.9%	99.3%	99.9%	100%
Maximum recovery	104%	109%	103%	105%
Minimum recovery	94.3%	94.5%	96.5%	96.0%
Failures	0	0	0	0
Count	826	1355	647	442
Sulfate				
Median recovery	98.9%	99.2%	99.6%	100%
Average recovery	98.9%	99.2%	99.6%	100%
Maximum recovery	109%	126%	103%	108%
Minimum recovery	88.5%	93.8%	96.4%	96.2%
Failures	0.121%	0.074%	0	0
Count	826	1355	647	442

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	-0.081%	0%	-0.001%	0.003%
Average RPD	-0.504%	-0.130%	0.187%	-0.024%
Max RPD	64.7%	200%	175%	97.8%
Min RPD	-129%	-200%	-38.8%	-71.6%
Count	1070	1070	1070	1070
Percentage of Failures	1.12%	0	0.467%	0.561%

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	100%	99.8%	100%	100%
Average Recovery	99.8%	99.4%	100%	100%
Max Recovery	124%	107.%	125%	130%
Min Recovery	1.34%	90.1%	-4.64%	7.29%
Count	674	674	674	674
Percentage of Failures	1.92%	1.33%	1.92%	1.78%

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	0.001 ppm	0.001 ppm	0.001 ppm
Maximum concentration	0.259 ppm	0.046 ppm	0.157 ppm	0.132 ppm
Minimum Concentration	0 ppm	0 ppm	0 ppm	0 ppm
Count	586	586	586	586
Percentage of Samples with Measured Concentrations Exceeding MDL	6.66%	4.61%	1.53%	3.07%

Table 6. Extraction QC check recoveries.

Chloride	Low	Mid	High
Median recovery	100.5%	100.5%	101%
Average recovery	100.6%	101%	101%
Maximum recovery	132%	178%	118%
Minimum recovery	92.1%	93.4%	94.3%
Count	224	274	318
Percentage with Recovery Outside Acceptable Range	1.33%	2.55%	0.314%
Nitrite	Low	Mid	High
Median recovery	97.7%	99.4%	99.6%
Average recovery	98.0%	99.8%	99.8%
Maximum recovery	108%	112%	109%
Minimum recovery	88.7%	92.1%	93.5%
Count	224	274	318
Percentage with Recovery Outside Acceptable Range	0.446%	0.364%	0
Nitrate	Low	Mid	High
Median recovery	98.6%	98.8%	99.9%
Average recovery	98.7%	99.0%	100%
Maximum recovery	106%	116%	104%
Minimum recovery	89.3%	92.8%	95.8%
Count	224	274	318
Percentage with Recovery Outside Acceptable Range	0.446%	0.364%	0
Sulfate	Low	Mid	High
Median recovery	98.6%	99.1%	101%
Average recovery	98.5%	99.3%	101%
Maximum recovery	104%	110%	108%
Minimum recovery	90.5%	94.0%	91.9%
Count	224	274	318
Percentage with Recovery Outside Acceptable Range	0	0	0

During 2017, we observed contamination in multiple method blanks and laboratory control spikes for 1 full batch and 1 partial batch of extracted samples. The contamination included chloride, nitrate, and sulfate, no nitrite was present. The method blanks showing contamination above acceptable limits were reanalyzed and we found that the contamination level increased, the average for chloride measured in the method blanks increased from 0.025 ppm to 0.038 ppm, the nitrate average increased from 0.014 ppm to 0.021 ppm and sulfate increased from 0.011 ppm to 0.024 ppm. This evidence suggested that the tops of the vials or caps may have been contaminated and evaporation following the original analysis led to higher results. We obtained XRF results for the impacted samples from the University of Davis and compared total sulfur/inorganic sulfate/3 ratios for all samples impacted and found minimal differences. All samples impacted were flagged for suspect contamination. We also reanalyzed all samples impacted and flagged samples as contaminated when differences between the two analyses exceeded 10%. About 15-20% of the samples showed some differences.

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. Figures 1a and 1b show the relative percent differenced measured for chloride as a function of concentration 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	0.010%	0%	0.03%	0.01%
Average RPD	-0.40%	-10.1%	-0.31%	-0.40%
Max RPD	200%	200%	200%	200%
Min RPD	-200%	-200%	-200%	-200%
% Failures	1.34%	0.09%	0	0.09%
Count	1112	1112	1112	1112

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.

Table 8. Average Extraction Efficiencies

	Chloride	Nitrite	Nitrate	Sulfate
Average Extraction Efficiency	98.3%	92.0%	96.8%	99.1%

Quality Assurance Standards

An external QA standard 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	0.145 ppm	0.482 ppm
Average Recovery	100%	103%	96.7%	96.6%
Median Recovery	99.9%	103%	96.7	96.6
Max Recovery	139%	141%	104%	106%
Min Recovery	80.7%	69.3%	87.9%	90.6%
Count	380	380	380	380

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	0.980 ppm
Average Recovery	101%	95.2%	97.7%	98.0%
Median Recovery	101%	95.2%	97.6%	97.8
Max Recovery	127%	131%	105%	103%
Min Recovery	89.8%	72.3%	93.1%	91.9%
Count	396	396	396	396

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	0.100 ppm	0.043 ppm	0.587 ppm	1.97 ppm
Average Recovery	101%	96.7%	97.9%	98.5%
Median Recovery	101	96.4%	97.8	98.4%
Max Recovery	109%	114%	103%	104%
Min Recovery	94.8%	82.9%	92.8%	94.3%
Count	391	391	391	391

External PT Study

Throughout 2017, 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 are calculated yearly and results may be viewed via the following website. https://bqs.usgs.gov/PCQA/Interlaboratory_Comparison/index.php

Significant Changes for Documentation

The Chromeleon software was upgraded from version 6.8 to version 7.2 beginning in October of 2017 (batch 2017-32). A complete batch of samples were analyzed using both versions of software and no discernable differences were observed in the data.