

Research Triangle Institute International
2016 Quality Assurance Report
NPS IMPROVE Ion Analysis

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Introduction

All samples analyzed follow the National Park Service (NPS)-approved RTI Anion Cation Analysis by Ion Chromatography (IC). Within 60 days of sample receipt, nylon filters received from the IMPROVE Operations Contractor (OC) are extracted, and then Ion Chromatography (IC) is used to analyze for chloride (Cl⁻), Nitrite (NO₂⁻), nitrate (NO₃⁻), and sulfate (SO₄²⁻). 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: Cl⁻ is calibrated from 0.010 ppm to 2.0 ppm while NO₂⁻, NO₃⁻, and SO₄²⁻ 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 (MDLs)

Table 1. MDLs

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

The following analytical sequence is queued for analysis once the calibration is complete: 50 field samples, extraction QC checks, three sets of replicate injection samples, two matrix spikes, and continuing calibration verification (CCV) standards.

Continuing Calibration Verification (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 using the following equation.

$$\% \text{ Recovery} = \frac{\text{Measured Analyte Concentration}}{\text{Target Analyte Concentration}} \times 100$$

Measured concentrations must be within $\pm 10\%$ of target values. 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 re-analyzed. Average CCV QC recoveries are shown in Table 2 for all ions.

Table 2. QC CCV recoveries

Chloride	Low	Mid	Mid-High	High
Median recovery	98.9%	99.6%	99.5%	99.7%
Average recovery	98.5%	99.3%	99.6%	99.7%
Maximum recovery	107 %	106%	103%	104%
Minimum recovery	91.4%	93.0%	95.9%	92.2%
n	597	923	243	242
Nitrite	Low	Mid	Mid-High	High
Median recovery	98.3%	99.2%	99.3%	97.6%
Average recovery	98.3%	99.4%	99.2%	98.4%
Maximum recovery	108%	110%	105%	107%
Minimum recovery	91.5%	92.7%	90.6%	90.5%
n	597	923	243	242
Nitrate	Low	Mid	Mid-High	High
Median recovery	98.3%	99.5%	100%	101%
Average recovery	98.2%	99.4%	100%	101%
Maximum recovery	104%	105%	105%	104%
Minimum recovery	92.9%	92.9%	96.7%	93.6%
n	597	923	243	242
Sulfate	Low	Mid	Mid-High	High
Median recovery	97.8%	99.0%	99.8%	101%
Average recovery	98.2%	99.3%	99.9%	101%
Maximum recovery	109%	104%	108%	107%
Minimum recovery	94.3%	93.4%	95.5%	96.3%
n	597	923	243	242

Replicate Samples

Replicate samples are sample extracts poured twice and measured sequentially in the analytical batch. They are used to by the IMRPOVE OC to calculate analytical precision. All analytical batches include 3 sets of replicate samples and 50 NPS samples. The relative percent difference for replicate samples are calculated using the equation:

$$\% \text{ Relative Percent Difference} = \frac{\text{Difference Between Replicates}}{\text{Average of Replicate Results}} \times 100$$

The RPD must be within $\pm 10\%$ when sample concentrations are greater than ten times the stated MDL. The RPD's must be $\pm 100\%$ when sample concentrations are at the MDL and up to ten times the stated MDL. Table 3 shows results for all replicate samples. When an RPD for a replicate sample fails to meet the stated criteria, the sample is reanalyzed to verify the concentration.

Table 3. Replicate samples relative percent differences.

Analyte	Chloride	Nitrite	Nitrate	Sulfate
Median RPD	1.78%	3.78%	0.93%	0.52%
Average RPD	3.99%	12.3%	1.75%	1.08%
Max RPD	96.4%	200%	24.3%	52.3%
Min RPD	0	0	0	0
n	640	640	640	640
Percentage of Failures	0.47%	0	0	0

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 analytes. Samples are repeated when spike recoveries fail and the reason for failure is unknown.

Table 4. Spike recoveries.

Analyte	Chloride	Nitrite	Nitrate	Sulfate
Median Recovery	99.4%	99.8%	99.6%	100%
Average Recovery	100%	99.4%	99.7%	101.1%
Max Recovery	226%	107%	121%	209%
Min Recovery	91.0%	90.1%	94.2	95.0%
n	419	419	419	419
Percentage of Failures	1.19%	0	0.24%	0.96%

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 QCs: laboratory control spikes (LCS) and method blanks (MB). LCS extraction QCs 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 QCs are added to the list of samples on the COC beginning with 2 extraction QCs before the first sample on the COC. Additional extraction QCs are added at a rate of 1-2 following every 25 samples. The extraction QCs are prepared at the time that NPS samples are extracted and so the extraction QCs 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.

Analyte	Chloride	Nitrite	Nitrate	Sulfate
Median Concentration	0 ppm	0 ppm	0 ppm	0 ppm
Average Concentration	0.006 ppm	0.007 ppm	0 ppm	0.003 ppm
Maximum concentration	0.027 ppm	0.045 ppm	0 ppm	0.038 ppm
Minimum Concentration	0 ppm	0 ppm	0 ppm	0 ppm
n	448	448	448	448
Percentage of Samples with Measured Concentrations Exceeding MDL	5.58%	3.57%	0	1.34%

Table 6. Extraction QC check recoveries.

Chloride	Low	Mid	High
Median recovery	99.0%	99.5%	99.1%
Average recovery	99.1%	99.1%	99.1%
Maximum recovery	140%	112%	104%
Minimum recovery	92.5%	92.5%	91.3%
n	113	131	141
Percentage with Recovery greater than 110%	0.89%	0.76%	0
Nitrite	Low	Mid	High
Median recovery	97.0%	98.5%	97.5%
Average recovery	96.9%	98.4%	97.9%
Maximum recovery	102%	106%	107%
Minimum recovery	89.8%	93.3%	90.6%
n	113	131	141
Percentage with Recovery greater than 110%	0	0	0
Nitrate	Low	Mid	High
Median recovery	97.1%	97.9%	99.1%
Average recovery	96.9%	97.9%	99.1%
Maximum recovery	102.%	105.%	103.%
Minimum recovery	92.1%	91.0%	93.7%
n	113	131	141
Percentage with Recovery greater than 110%	0	0	0
Sulfate	Low	Mid	High
Median recovery	96.3%	97.7%	98.6%
Average recovery	96.2%	97.4%	98.8%
Maximum recovery	100%	107%	106%
Minimum recovery	92.5%	93.6%	94.2%
n	113	131	141
Percentage with Recovery greater than 110%	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.

Table 7. Relative Percent Differences Measured for Reanalyzed Samples.

Analytes	Chloride	Nitrite	Nitrate	Sulfate
Median RPD	3.48%	0.011%	1.93%	1.04%
Average RPD	8.09%	38.9%	3.12%	1.85%
Max RPD	200%	200%	200%	200%
Min RPD	0.014%	0	0	0
n	544	544	544	544

Figures 1a and 1b show the relative percent difference measured for chloride as a function of concentration for all reanalyzed samples. Figure 1a presents the data at full scale and Figure 1b presents the data with different scaling to enhance the lower concentrations. There are no required data quality objectives for reanalysis samples, however, it would be expected that the precision between replicate samples would resemble the precision between reanalyzed samples. For example when concentrations are greater than ten times the current MDL of 0.005 ppm, it would be expected that precision would be within $\pm 10\%$ as is expected for duplicate precision. About 10.5% of samples reanalyzed would fail to meet this criteria. These differences are likely due to chloride contamination introduced during the sample process from extraction through analysis in the laboratory. Chloride contamination also occurs in method blanks for about 6% of the samples (Table 5). The randomness of the contamination makes it difficult to eliminate it from the routine sample analysis. However, we have taken steps to improve our processes to minimize the introduction of chloride into the samples. Extra steps are taken to thoroughly clean gloves and autosampler caps and vials used to analyze the samples on the IC systems.

Figure 1a. Chloride Relative Percent Difference as a Function of Concentration Measured During Reanalysis of Samples.

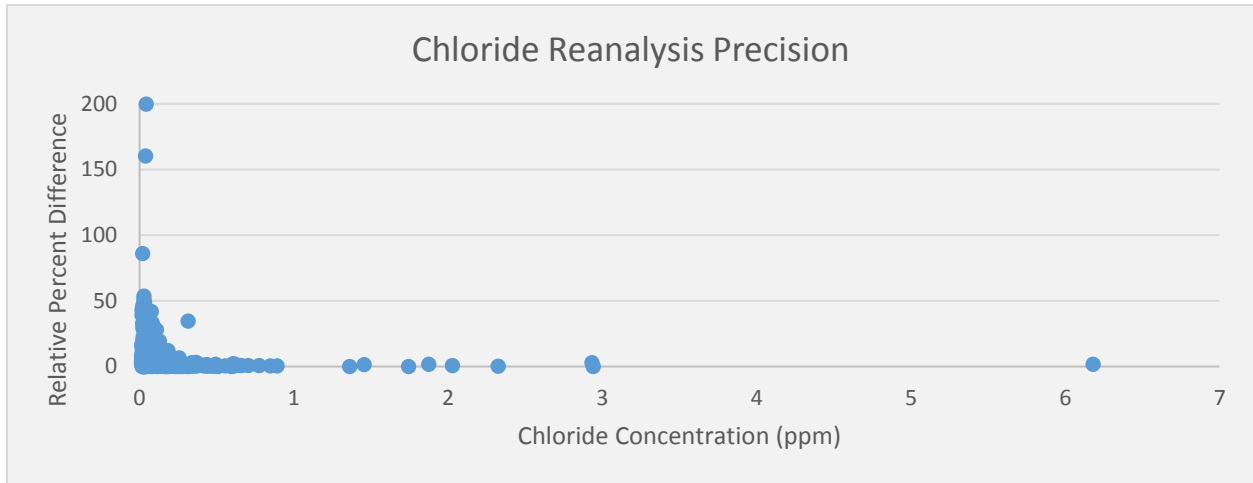
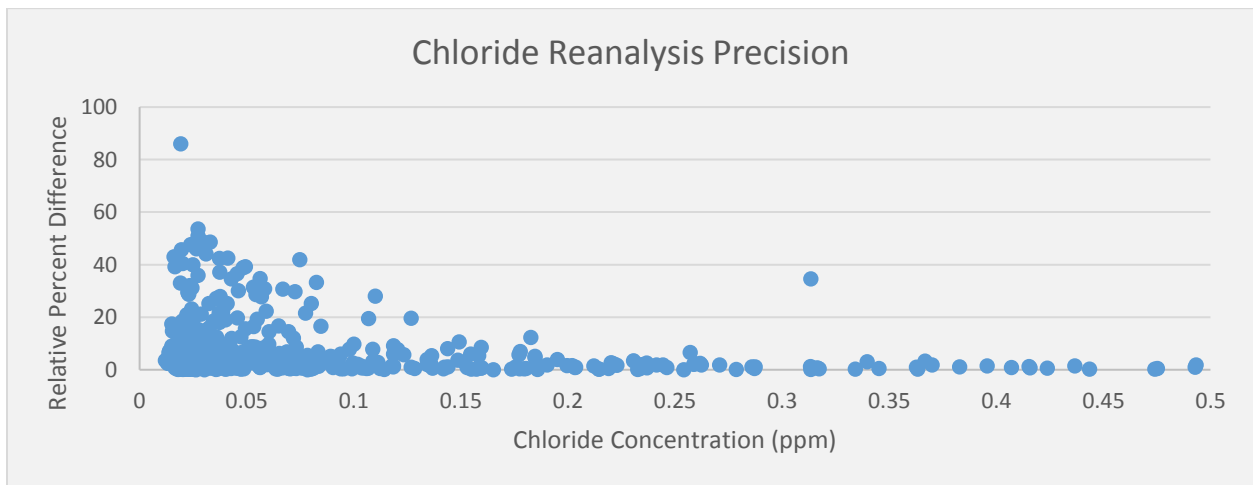
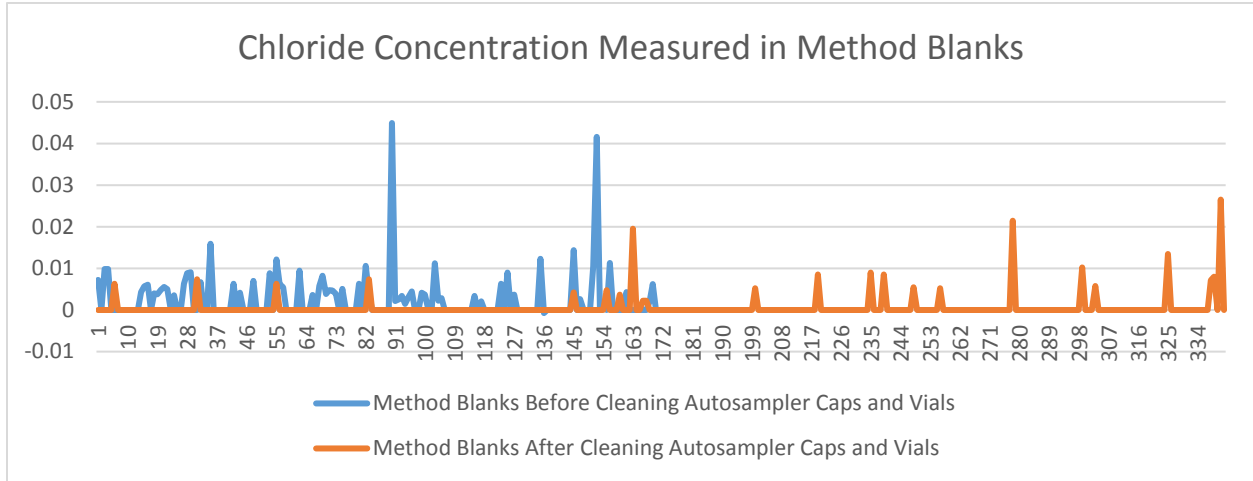


Figure 1b. Chloride Relative Percent Difference as a Function of Concentration Measured During Reanalysis of Samples.



As part of our evaluation of new procedures before their official introduction for the new contractual obligation, method blanks were introduced into the process for evaluation before beginning the new contract. Chloride was observed consistently in these method blanks, these observations led to introducing a cleaning step for the autosampler caps and vials. This step improved the amount and frequency of chloride detection in method blanks. Figure 2 compares chloride measured in extraction blanks before and after cleaning of the instrument caps and vials.

Figure 2. Comparison of Chloride Measured in Method Blanks Before and After Cleaning Instrument Caps and Vials.



Figures 3a and 3b show the relative percent difference measured for nitrite as a function of concentration for all reanalyzed samples. Figure 3a presents the data at full scale and Figure 3b presents the data with different scaling to enhance the lower concentrations. About 4% of the samples reanalyzed for nitrite would fail to meet the data quality objectives described for replicate sample analysis. We also observe about 4% of nitrite (Table 5) above the detection limit in extraction blanks. The introduction of cleaning steps for the autosampler caps and vials did not result in changes for the nitrite observed in method blank samples

Figure 3a. Nitrite Relative Percent Difference as a Function of Concentration Measured During Reanalysis of Samples.

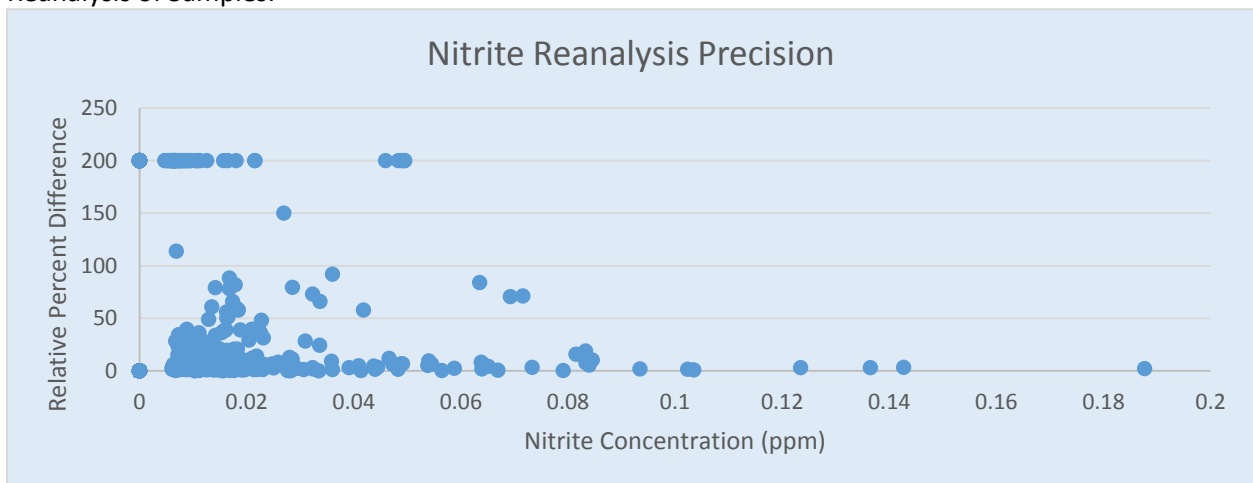


Figure 3b. Nitrite Relative Percent Difference as a Function of Concentration Measured During Reanalysis of Samples.

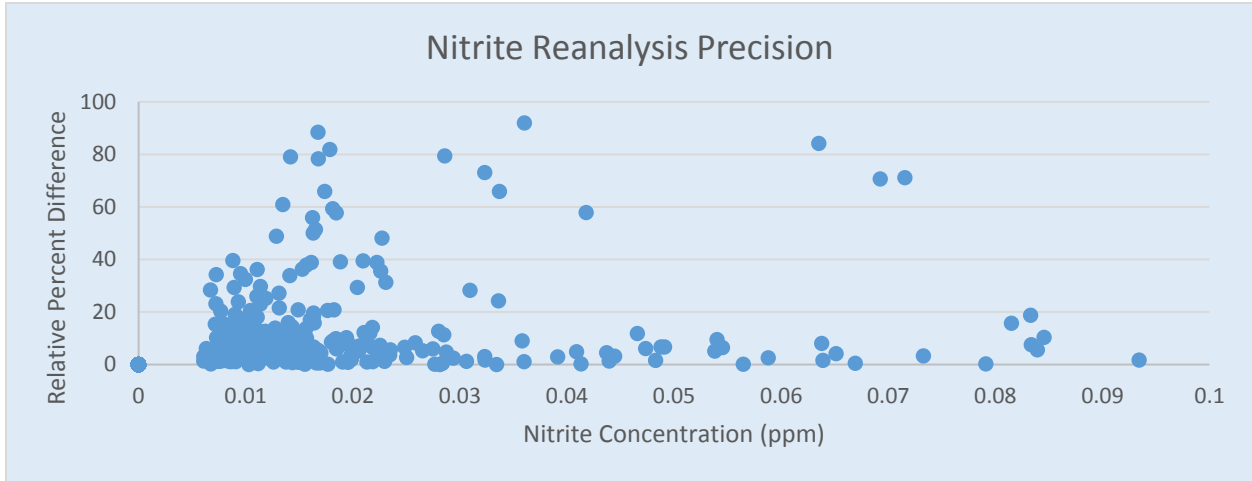


Figure 4 compares nitrite measured in extraction blanks before and after cleaning of the instrument caps and vials. There is not a significant difference between measurements before cleaning or after cleaning.

Figure 4. Comparison of Nitrite Measured in Method Blanks Before and After Cleaning Instrument Caps and Vials.

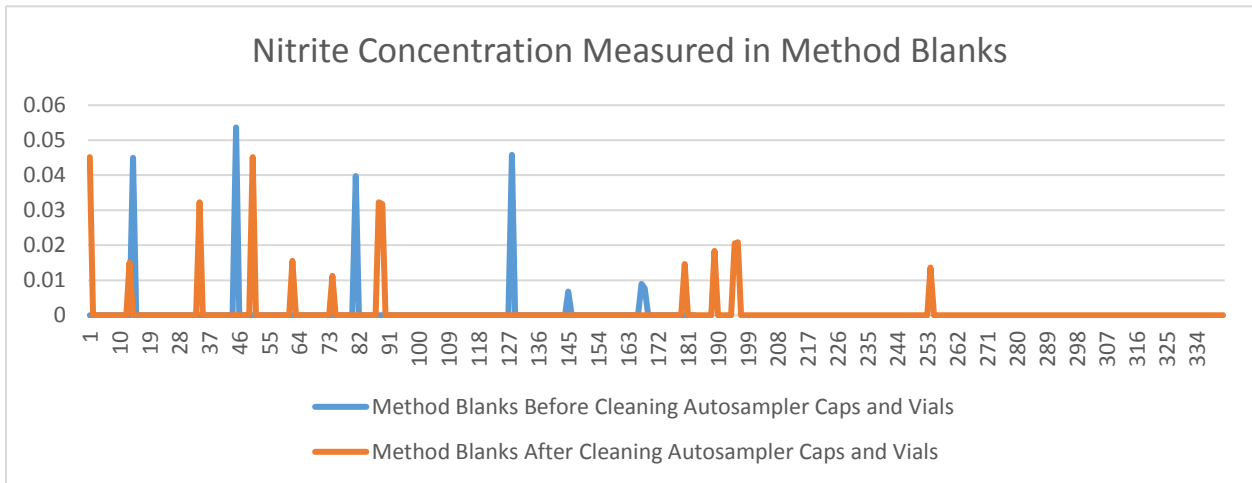


Figure 5a. Nitrate Relative Percent Difference as a Function of Concentration Measured During Reanalysis of Samples.

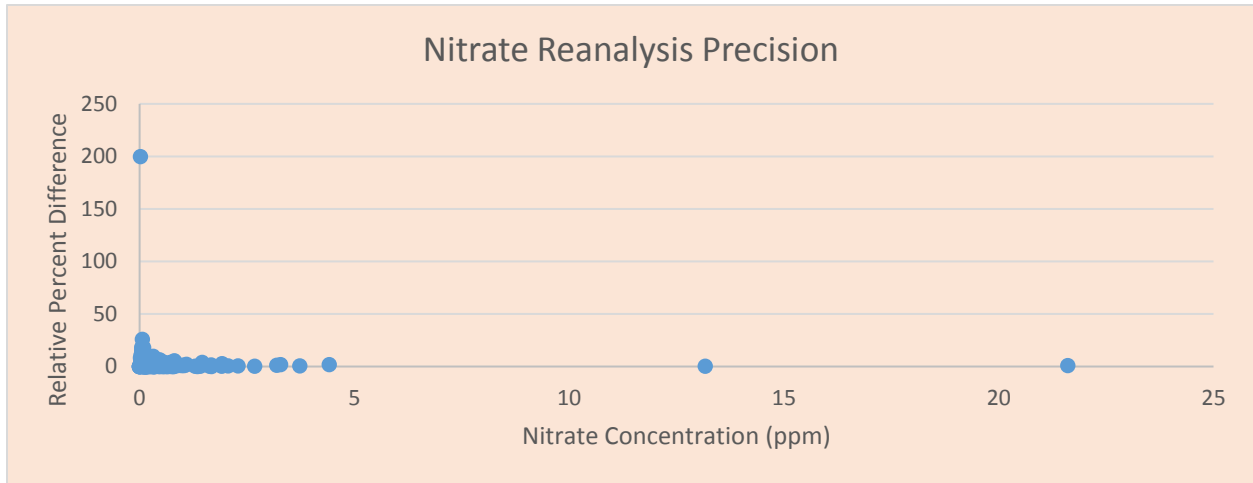
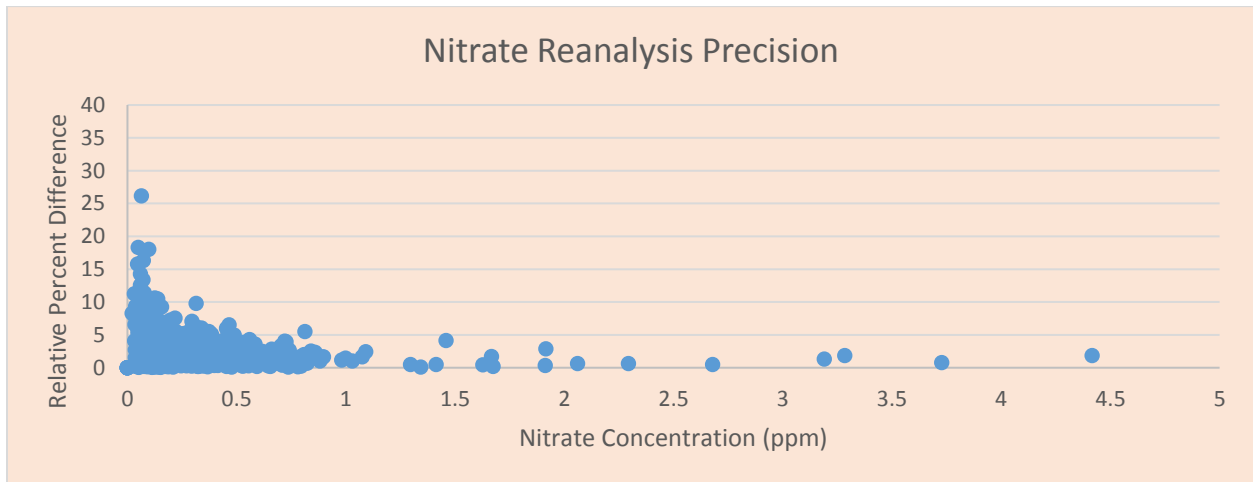


Figure 5b. Nitrate Relative Percent Difference as a Function of Concentration Measured During Reanalysis of Samples.



Figures 5a and 5b show the relative percent difference measured for nitrate as a function of concentration for all reanalyzed samples. Figure 5a presents the data at full scale and Figure 5b presents the data with different scaling to enhance the lower concentrations. The relative percent differences observed for nitrate currently meet the data quality objectives described for replicate samples. There has been no detection of nitrate in method blank samples (Table 5).

Figures 6a and 6b show the relative percent difference measured for sulfate as a function of concentration for all reanalyzed samples. Figure 6a presents the data at full scale and Figure 6b presents the data with different scaling to enhance the lower concentrations. The relative percent differences observed for sulfate also meets the current data quality objectives described for replicate samples.

Figure 6a. Sulfate Relative Percent Difference as a Function of Concentration Measured During Reanalysis of Samples.

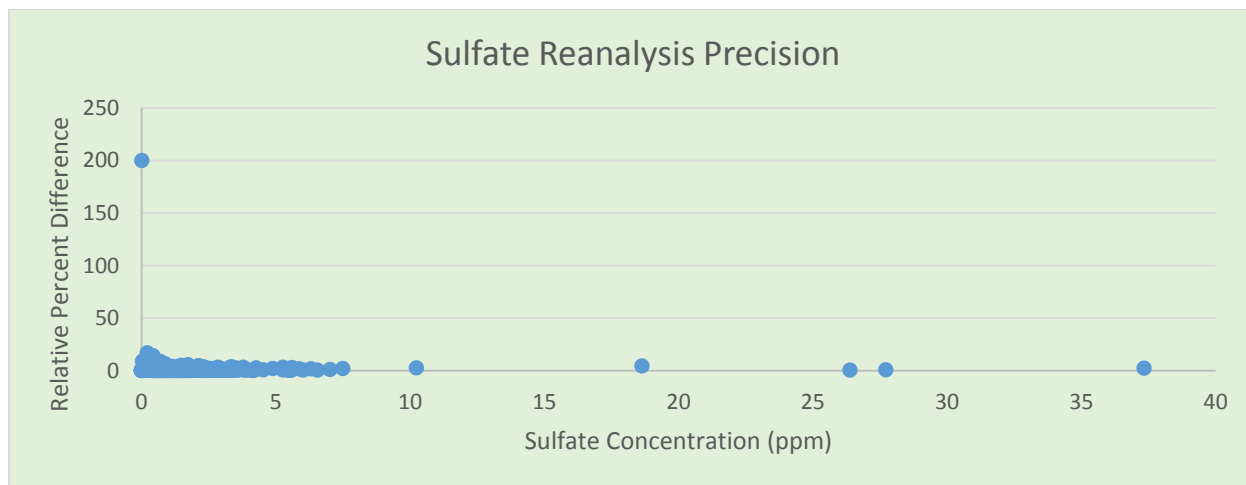
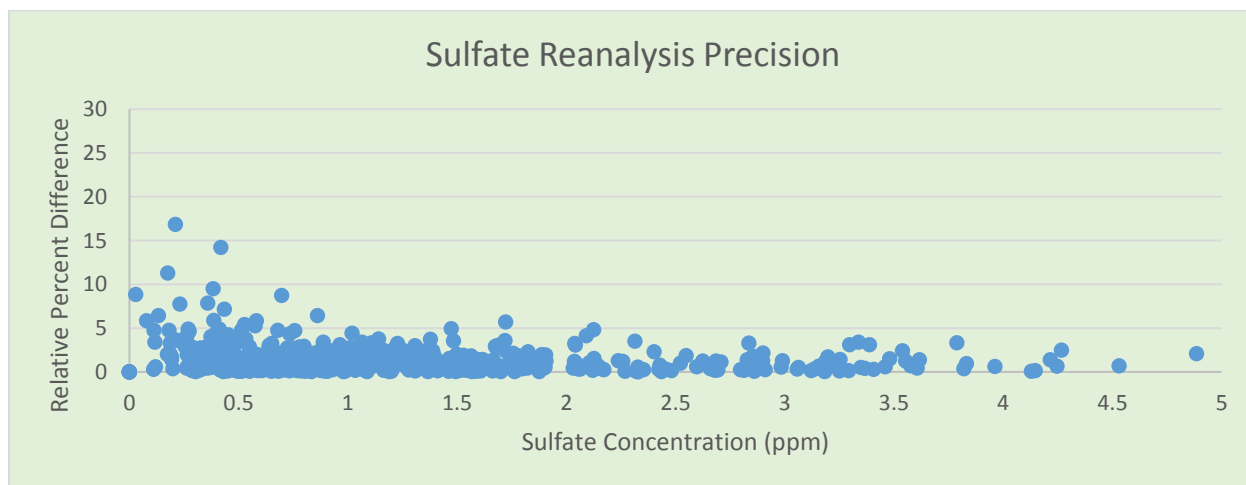


Figure 6b. Sulfate Relative Percent Difference as a Function of Concentration Measured During Reanalysis of Samples.



The random contamination observed for chloride and nitrite are not represented in the current MDLs and we are proposing a modification for MDL determination. Traditionally solutions used to calculate MDLs are analyzed back-to-back, poured by the same analyst, using the same calibration curve and instrument. Additional rigor and data quality could be added to the IMPROVE Network with no added cost by calculating analytically realistic MDLs that involve analysis on different days, with different

instruments, ambient conditions, calibration curves, and analysts. The variability measured in reanalysis samples is likely a far better representation of the variability observed for measurements across all samples for the network.

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

Analyte	Chloride	Nitrite	Nitrate	Sulfate
Average Extraction Efficiency	99.1%	92.9%	95.9%	99.8%

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. Table 9 shows target concentrations and RPDs for the 25th percentile solution.

Table 9. Target Concentrations and Relative Percent Differences 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	0.142 ppm	0.482 ppm
Average RPD	100%	102%	95.1%	96.6%
Max RPD	113%	123%	101%	101%
Min RPD	81.0%	86.9%	91.8%	92.8%
n	62	62	62	62

Table 10. Target Concentrations and Relative Percent Differences 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	0.050 ppm	0.022 ppm	0.287 ppm	0.977 ppm
Average RPD	100%	94.8%	95.8%	97.7%
Max RPD	108%	109%	98.8%	100%
Min RPD	92.5%	80.7%	91.7%	93.9%
n	60	60	60	60

Table 11. Target Concentrations and Relative Percent Differences 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	0.099	0.043 ppm	0.574 ppm	1.96 ppm
Average RPD	99.2%	95.9%	95.7%	97.8%
Max RPD	102%	103%	97.5%	99.3%
Min RPD	92.4%	87.4%	92.0%	94.6%
n	60	60	60	60

External PT Study

Throughout 2016, 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://bgs.usgs.gov/PCQA/Interlaboratory_Comparison/index.php

Significant Changes for Documentation

Batches from NPS set 36 through 39 were extracted by manually pipetting water into the extraction vials. Samples beginning with NOGA1 10/9/2016 from set 36 through samples ending with STAR1 11/02/2016 were extracted using pipettes. The auto delivery system developed a wiring problem and parts were replaced. The system was verified to be working correctly before use.