# 2020 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% | 101% | 102% |
| Maximum recovery | 256% | 112% | 109% | 107% |
| Minimum recovery | 97.0% | 95.0% | 95.1% | 93.8% |
| Failures | 0.23 % | 0.073% | 0% | 0% |
| Count | 879 | 1362 | 851 | 449 |
| | | | | |
| Nitrite | | | | |
| Median recovery | 95.9% | 97.9% | 99.6% | 101% |
| Average recovery | 96.1% | 98.0% | 99.6% | 101% |
| Maximum recovery | 248% | 108% | 109% | 109% |
| Minimum recovery | 90.2% | 91.7% | 94.0% | 98.5% |
| Failures | 0.34% | 0% | 0% | 0% |
| Count | 882 | 1368 | 852 | 449 |
| | | | | |
| Nitrate | | | | |
| Median recovery | 98.0% | 98.8% | 99.3% | 99.8% |
| Average recovery | 98.3% | 98.7% | 99.4% | 99.7% |
| Maximum recovery | 250% | 110% | 107% | 105% |
| Minimum recovery | 92.7% | 95.9% | 95.6% | 97.1% |
| Failures | 0.23% | 0% | 0% | 0% |
| Count | 878 | 1364 | 850 | 449 |
| | | | | |
| Sulfate | | | | |
| Median recovery | 98.6% | 99.3% | 99.5% | 101% |
| Average recovery | 98.9% | 99.3% | 99.5% | 101% |
| Maximum recovery | 251% | 110% | 108% | 106% |
| Minimum recovery | 95.1% | 96.0% | 96.3% | 96.0% |
| Failures | 0.11% | 0% | 0% | 0% |
| Count | 878 | 1364 | 852 | 449 |

## 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 are calculated by the difference divided by the average and 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 | 0.105% | 0% | 0.0978% | 0.0375% |
| Average RPD | 0.396% | 7.92% | 0.468% | 2.01% |
| Max RPD | 61.1% | 200% | 200% | 200% |
| Min RPD | -176% | -200% | -200% | -200% |
| Count | 1185 | 1185 | 1185 | 1185 |
| Percentage of Failures | 0.591% | 6.50% | 0.338% | 0.759% |

## 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% | 97.9 % | 101% | 100% |
| Average Recovery | 101% | 97.6% | 101% | 101% |
| Max Recovery | 113% | 105% | 144% | 124% |
| Min Recovery | 74.7% | 80.7% | 92.3% | 88.3% |
| Count | 826 | 826 | 826 | 826 |
| Percentage of Failures | 0.24% | 2.06% | 0.97% | 0.73% |

## 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 | 0.001 ppm | 0.001 ppm | 0.0002 ppm | 0.0007 ppm |
| Maximum concentration | 0.045 ppm | 0.067 ppm | 0.015 ppm | 0.060ppm |
| Minimum Concentration | 0 ppm | 0 ppm | 0 ppm | 0 ppm |
| Count | 649 | 649 | 649 | 649 |
| Percentage of Samples with Measured Concentrations Exceeding MDL | 4.9% | 2.8% | 1.2% | 1.1% |

Table 6. Extraction QC check recoveries.

| Chloride | Low | Mid | High |
|---|---|---|---|
| Median recovery | 101% | 101% | 101% |
| Average recovery | 101% | 100% | 101% |
| Maximum recovery | 255% | 108% | 126% |
| Minimum recovery | 94.4% | 43.1% | 85.2% |
| Count | 247 | 295 | 351 |
| Percentage with Recovery Outside Acceptable Range | 1.6% | 0.3% | 1.1% |

| Nitrite | Low | Mid | High |
|---|---|---|---|
| Median recovery | 94.2% | 96.6% | 100% |
| Average recovery | 94.3% | 96.7% | 100% |
| Maximum recovery | 100% | 106% | 105% |
| Minimum recovery | 89.7% | 40.5% | 82.8% |
| Count | 248 | 295 | 351 |
| Percentage with Recovery Outside Acceptable Range | 2.0% | 0.7% | 0.6% |

| Nitrate | Low | Mid | High |
|---|---|---|---|
| Median recovery | 97.0% | 97.6% | 98.7% |
| Average recovery | 96.9% | 97.5% | 98.8% |
| Maximum recovery | 101% | 105% | 103% |
| Minimum recovery | 92.9% | 41.4% | 81.6% |
| Count | 248 | 295 | 351 |
| Percentage with Recovery Outside Acceptable Range | 0% | 0.7% | 0.6% |

| Sulfate | Low | Mid | High |
|---|---|---|---|
| Median recovery | 97.9% | 98.8% | 100% |
| Average recovery | 97.8% | 98.5% | 100% |
| Maximum recovery | 106% | 108% | 106% |
| Minimum recovery | 90.8% | 42.4% | 81.8% |
| Count | 248 | 295 | 352 |
| Percentage with Recovery Outside Acceptable Range | 0% | 0.7% | 0.6% |

## 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 | -0.29% | 0% | 0.15% | 0.19% |
| Average RPD | -0.20% | 4.7% | 0.75% | -1.1% |
| Max RPD | 145% | 200% | 200% | 200% |
| Min RPD | -200% | -200% | -200% | -200% |
| % Failures | 1.5% | 0.13% | 1.3% | 0.89% |
| Count | 1577 | 1578 | 1577 | 1578 |

## 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 | 105% | | 101% | 100% |

## 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 | 0.026 ppm | 0.011 ppm | 0.144 ppm | 0.489 ppm |
| Average Recovery | 105% | 98.5% | 96.2% | 97.8% |
| Median Recovery | 105% | 97.7% | 96.4% | 98.2% |
| Max Recovery | 128% | 160% | 109% | 105% |
| Min Recovery | 61.0% | 0% | 79.4% | 64.4% |
| Count | 440 | 439 | 444 | 445 |

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

| QA50 | Chloride | Nitrite | Nitrate | Sulfate |
|---|---|---|---|---|
| Target Concentration | 0.050 ppm | 0.023 ppm | 0.300 ppm | 1.00 ppm |
| Average Measured Concentration | 0.052 ppm | 0.021 ppm | 0.290 ppm | 0.987 ppm |
| Average Recovery | 104% | 94.9% | 96.8% | 98.7% |
| Median Recovery | 104% | 95.2% | 97.0% | 99.1% |
| Max Recovery | 147% | 130% | 103% | 107% |
| Min Recovery | 62.1% | 0% | 78.9% | 49.3% |
| Count | 442 | 441 | 445 | 445 |

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

| QA75 | Chloride | Nitrite | Nitrate | Sulfate |
|---|---|---|---|---|
| Target Concentration | 0.100 ppm | 0.045 ppm | 0.600 ppm | 2.00 ppm |
| Average Measured Concentration | 0.104 ppm | 0.042 ppm | 0.584 ppm | 1.98 ppm |
| Average Recovery | 104% | 93.7% | 97.3% | 99.1% |
| Median Recovery | 104% | 93.9% | 97.4% | 99.5% |
| Max Recovery | 323% | 169% | 105% | 108% |
| Min Recovery | 0% | 0% | 0% | 0% |
| Count | 441 | 438 | 441 | 441 |

## External PT Study

Throughout 2020, 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

## Significant Changes for Documentation

RTI acquired 4 new Aquion systems and 3 new AS-AP autosamplers and one ICS-6000 system. The systems were evaluated for suitability by conducting replicate analyses of samples on the existing and new systems. Two of the Aquion systems are configured for anion analysis and will be identified in future analysis as A11, placed into operation on January 1, 2020 and A12, placed into operation on March 24, 2020. The ICS-6000 system is currently supporting research and development of Organic sulfur species.

## Documentation of Suspected Chloride Interference

During our investigation of organic sulfate (OS) by IC, the OS standard 2-methyltetrol sulfate (2MTS) was observed to interfere with chloride retention time when using the carbonate/bicarbonate IC method (Figure 1)

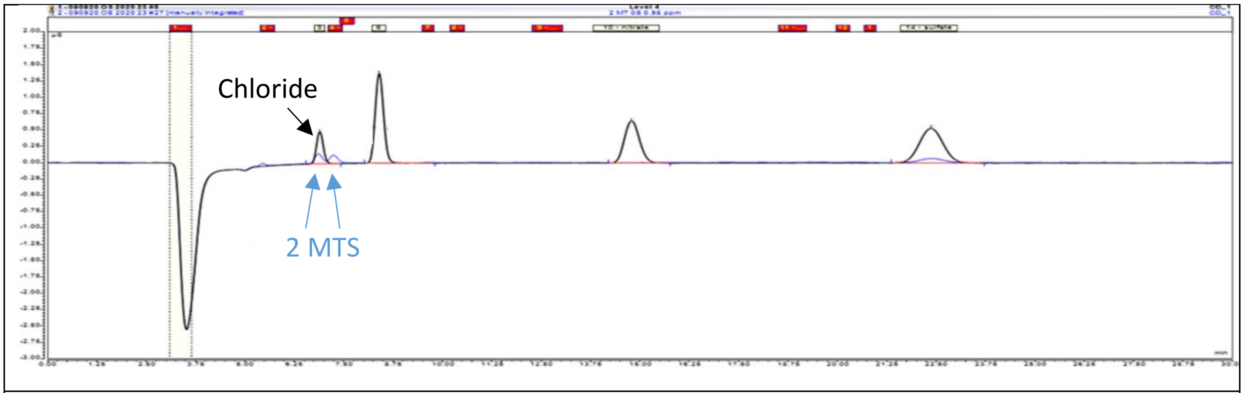

Figure 1. Observed retention time for synthesized 2MTS outlined in blue, (2 isomers) and chloride outlined in black measured by IC using carb/bicarb eluent.

Since 2MTS is known to be the most abundant OS species formed from multiphase reactions with epoxidiols (IEPOX) in the presence of acidic sulfate aerosols,[9,10] we began reanalyzing samples with evidence of this peak. To facilitate these measurements, we developed and applied an IC method utilizing a KOH eluent to achieve near baseline resolution of 2 MTS from chloride (Figure 2).

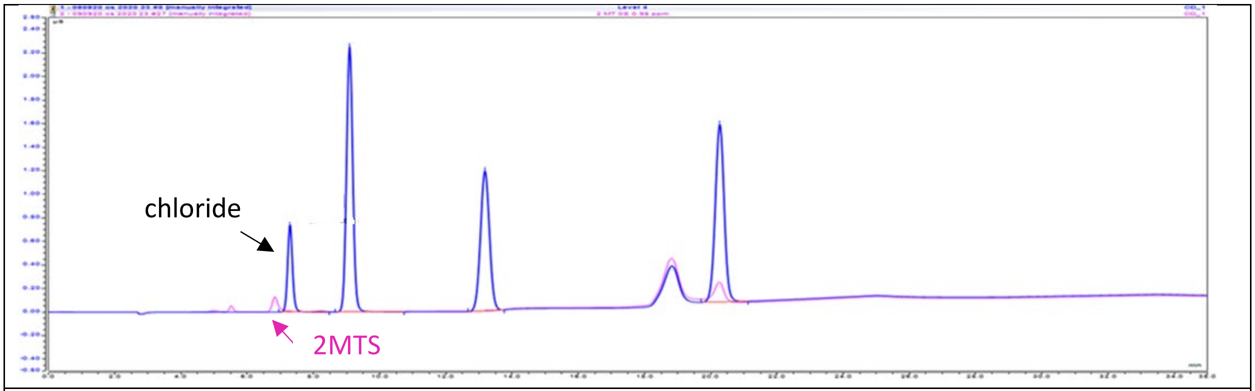

Figure 2. Resolution of 2 MTS outlined in pink and Chloride outlined in blue measured by IC using KOH method.

A dual IC instrument was configured with one system utilizing the carb/bicarb eluent matching the typical analysis method for IMPROVE and CSN samples, and the second system utilizing KOH as the eluent prepared via eluent generation for gradient concentrations. The dual system is equipped with an autosampler with a divertor valve so that the sample extracts can be analyzed by each separation method.

A comparison of the original chloride results (reported) with values obtained through reanalysis by both methods is presented in Figure 3.

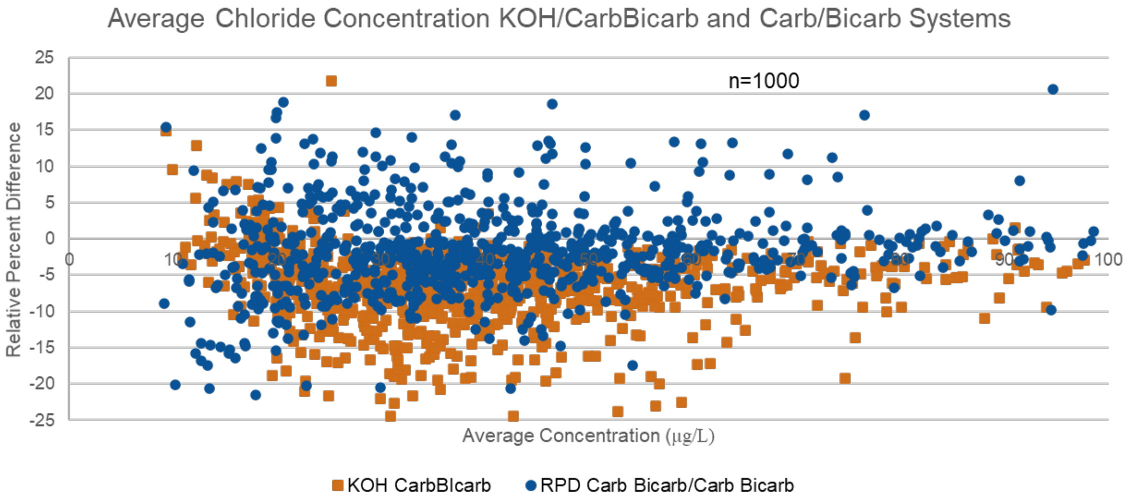

Figure 3. Relative percent difference calculated between original and reanalysis results as a function of concentration determined in samples measured using the existing approved carb/bicarb method and the modified gradient KOH eluent method (orange) and samples measured on different instruments using the existing approved carb/bicarb method (blue).

A bias of approximately 10 – 15% was observed for relative percent differences between the KOH/Carb Bicarb and Carb/Bicarb compared to Carb/Bicarb reanalysis. For the n = 1,000 test samples, this corresponded to a maximum concentration difference of 5 ppb for samples with chloride concentrations of approximately 100 ppb and above, and roughly 3 ppb for samples with chloride concentrations at the 25 ppb level.

A likely chloride interference was observed by RTI while conducting a collaborative research study exploring the prevalence of OS compounds and their impact on sulfur measurements. It is hypothesized that the impact of the observed bias will vary seasonally and regionally as a function of the 2MTS (OS) and chloride concentrations. Samples analyzed during 2020 were flagged when evidence of 2MTS was present in the chromatogram. We are continuing to evaluate data from subsequent dual analyses to fully investigate the impact and ways to flag data for future analyses.