Standard Operating Procedures
RTI SOP # Ions1

Determination of Anions and Cations Extracted from Nylon® Filters by Ion Chromatography

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SEE LAST PAGE OF SOP FOR REVIEW AND REVISION HISTORY

Table of Contents

Page

TABLE OF TABLES

1.0 SCOPE AND APPLICATION

The method described will be used for the quantitative determination of anions (defined as chloride (Cl^-), nitrate (NO_3^-), and sulfate (SO_4^{2-})) and cations (defined as sodium (Na^+), ammonium (NH_4^+), and potassium (K^+)), levels in air quality samples collected on Nylon® filters and for background evaluations of new filter batches. The method will be conducted in accordance with applicable SOPs cited herein. The method is suitable for extracting and analyzing samples following IHPAT accreditations requirements. Samples will be processed by extracting each filter with deionized water. Deionized water will be added using the SimPrep Autodilutor. The samples will be sonicated for 60 minutes following the addition of deionized water and shaken for 8 hours while at ~4 degrees Celsius (°C) and allowed to sit overnight at ~ 4°C. The analysis will be performed after samples have been removed from the shaker table. The extracts will be analyzed for anions and cations using ion chromatography (IC).

2.0 SUMMARY OF THE METHOD

Nylon filters used for collection of anions and cations do not require pre-treatment and are extracted with deionized water. Extraction with deionized water makes it possible to analyze for both anions and cations.

Sample extracts are passed through columns coated with quaternary ammonium active sites for anion analysis and through columns coated with carboxyl active sites for cation analysis. During passage through the column, ion separation occurs due to the different affinities of the ions at the active resin sites. Following separation, the ions pass through suppressors which lower background levels of eluent ions. Species are detected and quantified by a conductivity detector. Accuracy and precision will be monitored routinely by analysis of quality control (QC) samples.

3.0 DEFINITIONS

- **QA**–Quality Assurance. QA is a process that is used to maintain a desired level of quality in a service.
- **QC**–Quality Control. QC is a system of maintaining standards in testing by comparing against specified outputs.
- **QCS**–Quality Control Standards. QCSs are prepared in DI water and spiked with a known concentration at low, mid and high range as applicable to the calibration and are used to verify the calibration curve.

- **DI Water**–Deionized Water. For reagent water, 18.2 MΩ of DI water is used from the Milli-Q system.
- **SOP**–Standard Operating Procedure. SOPs are established methods to be followed routinely for the performance of designated operations.
- **CSN –** Chemical Speciation Network**.**
- **IHLAP** – Industrial Hygiene Laboratory Accreditation Program – The Ions laboratory is accredited for analysis conducted under the IHLAP program.
- **LCS**–Laboratory Control Spike. The purpose of an LCS is to evaluate accuracy and precision for the entire process from extraction through analysis and used for calculating uncertainty when reporting data under IHLAP accreditation.
- **MB**–Method Blank. The purpose of an MB is to evaluate contamination of the overall process, including sample preparation.
- **SPK**– Matrix Spike. The purpose of an MS is to determine whether the sample matrix contributes bias to the analytical result. The MS is an aliquot of an environmental sample to which known quantities of the method analytes are spiked in the sample.
- **DUP** – Duplicate samples are used to measure uncertainty during the analysis of samples. A duplicate samples is the same sample poured into two distinct analytical vials and analyzed consecutively in the analytical batch.
- **Analytical Batch** – A sample queue containing a total of at least 50 field generated samples, QC's at a rate of at least 1 per every 10 samples, SPK and DUP's at a rate of 1 per every 20 samples, LCS's prepared during the extraction step at a rate of 1 per every 20 samples and MB samples prepared during the extraction at a rate of 1 per every 30 samples.
- **USB**–Universal Serial Bus. The USB drive is standardized technology for attaching peripheral devices to a computer.
- **HDPE**–High Density Polyethylene
- **ACS**–American Chemical Society
- **NIST**–National Institute of Standards & Technology
- **MDL**–Method Detection Limit. An MDL is the minimum concentration of an analyte that can be measured and reported with 99% confidence that the measured concentration is distinguishable from method blank results.
- **IDL**–Instrument Detection Limit. The IDL is the concentration equivalent to a signal, due to the analyte of interest, which is the smallest signal that can be distinguished from background noise by a particular instrument.

4.0 INTERFERENCES AND CONTAMINATION CONTROL

Contaminants in reagents, plastic labware and other components of sample processing, as well as environmental sources, typically have the potential to cause erroneously high results. Therefore, all samples, quality control standards and calibration standards will be prepared in plastic labware rinsed with deionized (DI) water. Analysts will use gloves rinsed in DI water when handling filters, extracts, calibration standards and QC standards. Samples will be capped following the addition of DI water and will not be uncapped except during the measurement procedure. Samples will be recapped as soon as possible after they are aliquoted for analysis.

Integration tools are used eliminate chromatographic interferences such as shoulder peaks and co-eluting peaks. Samples are diluted when ion concentrations are so high that they interfere with resolution of adjacent ion peaks.

5.0 HEALTH AND SAFETY WARNINGS

All laboratory personnel involved in handling, transporting, and measurement of these samples will wear gloves and eye protection with side shields, in addition to following the normal safety requirements in the RTI Safety and Occupational Health Manual.

6.0 SAMPLE RECEIPT, STORAGE AND RECORDKEEPING

Filters to be inventoried will be stored at < -0 degrees Celsius (°C) or colder in a freezer until extraction. Unique laboratory numbers assigned by the sample handling laboratory will be recorded on the Sample Tracking and Extraction Log . A Sample Receipt Form (see **Figure 1** for an example of the sample receipt form) will be filled out when samples are received by the laboratory. These records will accompany the samples from the point of extraction through analysis. Samples will be extracted at room temperature and stored at ~4°C overnight following extraction. Unused sample portions will be stored in a refrigerator for a minimum of 6 months beginning from the archival date. Samples will be disposed when data have been transferred and validated by UC Davis.

7.0 EQUIPMENT, REAGENTS, AND MATRIX

7.1 Laboratory Equipment

7.1.1 Labware

- Volumetric flasks, Nalgene, various sizes

- Pipette tips, clear plastic, disposable
- Ion chromatography vials (SCP Science, Scientific Sales)
- Storage bottles of various sizes, HDPE or Teflon
- Disposable flat bottom digestion vials with screw caps, 50 milliliter (mL), polypropylene (Moldpro)
- Graduated cylinders, polymer and glass, various sizes
- Tweezers

7.1.2 Equipment

- Micropipettes (micropipettes), fixed and variable volume
- Traceable thermometers with calibration that complies with ISO/IEC 17025, ANSI/NCSL Z540-1 and 9001 standards. The uncertainty will be evaluated at the time of receipt of the thermometers. If the uncertainty exceeds the estimated uncertainty associated with the daily laboratory measurement 4° C ± 6°C a correction factor will be determined and applied to the reading.
- Refrigerator (~4°C)
- Freezer (≤0ºC, nominal)
- Analytical balance capable of one (1) gram (g) readability
- Analytical balance capable of two decimal place (.01) g readability
- Ultrasonic bath fitted with epoxy-coated test tube rack to hold centrifuge tubes
- Glove Box and access to Nitrogen
- SimPrep Autodilution System (SimPrep)
- Ion Chromatography (Dionex ICS-2000, ICS-3000, ICS-6000 & Aquion) systems
    - Analytical and Guard columns – the serial number of the analytical column will be included in the instrument logbook when columns are changed to provide traceability.
- Suppressors

7.1.3 Reagents and Standards

- 18.2 megaohm (MΩ) DI water (DI)
- 5.0N $H2SO_4$ (sulfuric acid), Scientific sales or equivalent.

- Standard stock may be commercially purchased for each anion or cation. The manufacturer's expiration date and storage conditions must be observed. . Upon the first time that stock standard is opened for use, the analyst will verify that the certified value concentrations are within ± 3% of the nominal value. If certified values are outside of the 3%, the stock standard will not be used. The nominal concentration will be used to calculate standard calibration and QC sample concentrations. A solution prepared from a stock standard will not have an expiration date past the certified date of the stock standard. Stock standards used for this method include the following:
  - Na^+ stock standard, 1,000 parts per million (ppm) and NIST traceable. Two sources for calibration and QC samples (NSI Lab Solutions, Spex CertiPrep, or other approved vendor).
  - NH_4^+ stock standard, 1,000 ppm and NIST traceable. Two sources for calibration and QC samples (NSI Lab Solutions, Spex CertiPrep, or other approved vendor).
  - K^+ stock standard, 1,000 ppm and NIST traceable. Two sources for calibration and QC samples (NSI Lab Solutions, Spex CertiPrep, or other approved vendor).
  - Cl^- stock standard, 1,000 ppm and NIST traceable. Two sources for calibration and QC samples (NSI Lab Solutions, Spex CertiPrep, or other approved vendor).
  - NO_3^- stock standard, 1,000 ppm and NIST traceable. Two sources for calibration and QC samples (NSI Lab Solutions, Spex CertiPrep, or other approved vendor).
  - NO_2^- stock standard, 1,000 ppm and NIST traceable. Two sources for calibration and QC samples (NSI Lab Solutions, Spex CertiPrep, or other approved vendor).
  - SO_4^- stock standard, 1,000 ppm and NIST traceable. Two sources for calibration and QC samples (NSI Lab Solutions, Spex CertiPrep, or other approved vendor).
- Na_2CO_3 (Fisherbrand)
- Na_2HCO_3 (EMD)

7.2 Preparation of Labware

7.2.1 General Plastic Labware

- Volumetric labware will be filled with DI water and stored capped/covered.
- Devices such as plastic rods and spatulas for aliquoting samples will be rinsed in DI water.

7.2.2 Pipette Tips, Plastic

- Only plastic pipette tips that are free of Ions contamination will be used. If quality control blank analyses consistently show measurable Ions, contamination due to the pipette tip will be considered.

7.2.3 Autosampler Tubes

- Vials for use with AS40 autosamplers are available commercially and are rinsed 3 times with DI water and dried before use. Vials for use with AS-AP autosamplers are used as received.

7.2.4 SimPrep Autodilutor DI Water

- The container used to deliver DI water into the vials for extraction will be rinsed and refilled prior to beginning the extraction. The reading for polisher DI reading is 18.2 MΩ. When the reading drops below this level, DI will not be used until filters have been changed and the water quality reaches 18.2 MΩ.

7.3 Micropipettes

Micropipettes used in this analysis will be calibrated in accordance with RTI SOP 100-EQP-020.5: *Gravimetric Calibration Verification and Maintenance of Liquid Dispensing Devices*. No uncalibrated pipettes will be used for transfers that are intended to be quantitative.

7.4 Refrigerator and Freezer

Any refrigerator and freezer used for this work will be maintained in accordance with RTI SOP 100-EQP-007.7: *Refrigerator and Freezer Monitoring, Maintenance and Operation with Storage Condition Definitions* and RTI SOP 100-EQP-009.7: *Calibration of Temperature Measuring Devices*. The freezer will be set at <0°C (nominal) at all times for the samples.

7.5 Analytical Balance

Any analytical balance used for this work will be calibrated and maintained in accordance with RTI SOP 100-EQP-004.6: *Calibration, Use and Maintenance of Balances*.

7.6 SimPrep Autodilution system

The SimPrep Autodilution system will be maintained in accordance with RTI SOP Ions3: *Filter Extraction via SimPrep Autodilution System.*

7.7 Reagents

7.7.1 Anion Chromatography Reagents Preparation

Note: Use ACS reagent-grade chemicals and 18.2 MΩ-cm DI water for the preparation of all solutions.

1. Concentrated eluent (100X), 30 mM $NaHCO_3$/270 mM Na_2CO_3: Dissolve 2.5209 g $NaHCO_3$ and 28.6178 g Na_2CO_3 in 1L of DI water. (Note: Do NOT dry the salts that are used to prepare the eluent.)
2. Working eluent, 0.3 mM $NaHCO_3$/2.7 mM Na_2CO_3: Dilute 200 mL concentrated eluent to 20 L with DI water.
3. Regenerant, 0.025 N H_2SO_4: Dilute 100 mL of 5.0 N H_2SO_4 to 20 L with DI water. (Note: This reagent is not used for an IC system equipped with a self-regenerating suppressor.)

7.7.2 Anion Calibration and Quality Control (QC) Standards

Note: Calibration standards are prepared from a commercially purchased National Institute of Standards and Technology (NIST)-traceable stock standard (SPEX CertiPrep or a verified source) and QC standards are prepared from commercially purchased NIST-traceable stock standards (NSI stock standards or a verified source). Two different sources should always be used when preparing the calibration and QC standards.

- Anion stocks purchased from SPEX CertiPrep, 1000 ppm each for chloride, nitrate, and sulfate.
- Anions stocks purchased from NSI, 1000 ppm each for chloride, nitrate, and sulfate.

7.7.3 Cation Chromatography Reagents

Note: Use ACS reagent-grade chemicals and 18.2 MΩ-cm DI water for the preparation of all solutions.

- Concentrated eluent stock solution: 5 N H_2SO_4, purchased from Scientific Sales.
- Working eluent, 22 mN H_2SO_4: Dilute 4.4 mL 5 N H_2SO_4 to 1 L using DI water.

7.7.4 Cation Calibration and Quality Control (QC) Standards

Note: Calibration standards are prepared from commercially purchased NIST-traceable stocks (SPEX CertiPrep or a verified source) and QC standards are prepared from commercially

purchased NIST-traceable stock standards (NSI stock standards or a verified source). Two different sources should always be used when preparing the calibration and QC standards.

- Cation stocks from SPEX CertiPrep, 1000 ppm each for sodium, ammonium, and potassium.
- Cations stocks purchased from NSI 1000 ppm each for sodium, ammonium, and potassium.

8.0 STANDARD AND SAMPLE PREPARATION

8.1 Quality Control Standards

Quality control standards (QCS) are prepared in DI water and spiked with known concentrations at low, mid and high range as applicable to the calibration. The QCS are used to initially verify the calibration and continue to verify the calibration throughout the analysis run. The QCS are prepared using the intermediate anion and cation QC standards.

Intermediate Anion QC Standard and Intermediate Cation QC Standard Intermediate solutions are stable for at least six (6) months from the date of preparation.

Anions 1000 ppm, NIST-traceable, commercially purchased SO_4^{2-}, NO_3-, and Cl- solutions will be used to prepare the intermediate anion QC standard. A 15.0 mL aliquot of 1000 parts per million (ppm) SO_4^{2-}, a 7.5 mL aliquot of the 1000 ppm NO_3-, and a 2.5 mL aliquot of the 1000 ppm Cl- will be diluted to 250 mL in DI water to prepare a 60 ppm SO_4^{2-}, 30 ppm NO_3-, and 10 ppm Cl- intermediate anion QC standard. A list of QC standards and concentrations for each of the ions are shown in **Table 1**.

Table 1. Anion QC Standards

Anions	Volume of Intermediate QC Standard added (mL)	Diluted Volume (mL)	Final Concentration SO_4^{2-} (mg/L)	Final Concentration NO_3^- (mg/L)	Final Concentration Cl^- (mg/L)
QC LOW	2.00	100	1.20	0.60	0.20
QC MED	12.5	250	3.00	1.50	0.50
QC MED HI	10.0	100	6.00	3.00	1.00
QC HIGH	20.0	100	12.0	6.00	2.00

Cations 1000 ppm, NIST-traceable, commercially purchased Na^+, K^+, and $NH4^+$ solutions will be used to prepare the intermediate cation QC standard. A 10.0 mL aliquot of 1000 ppm Na^+, K^+, and $NH4^+$ will be diluted to 100 mL in DI water to prepare the 100 ppm Na^+, K^+, and $NH4^+$ intermediate cation QC standard. A list of QCS and concentrations for each of the ions are shown in **Table 2**.

Table 2. Cations QC Standards

Cations	Volume of Intermediate QC Standard added (mL)	Diluted Volume (mL)	Final Concentration Na^+, K^+, NH_4^+ (mg/L)
QC Low	0.020	100	0.200
QC Med	0.250	100	0.250
QC Med Hi	0.750	100	0.750
QC High	2.000	100	2.000

Laboratory Control Samples (LCS) are prepared during the extraction of the samples by pipetting known concentrations into 50 mL centrifuge tubes and diluting them with the same volume of DI water used to extract filters. Target concentrations for LCS solutions are listed in **Table 3**.

Table 3. Target Concentrations for Anions in LCS Solutions

Final Conc. (ppm)	Final Volume (mL)	LCS spiking Solution Concentration (ppm)	LCS spiking Solution Aliquot (mL)
LCS low **Cl^-** = 0.196 **$N0_3^-$** = 0.588 **$S0_4^{2-}$** = 1.18	25.500	**Cl^-** = 10 **$N0_3^-$** = 30 **$S0_4^{2-}$** = 60	0.500
LCS med **Cl^-** = 0.476 **$N0_3^-$** = 1.43 **$S0_4^{2-}$** = 2.86	26.250	**Cl^-** = 10 **$N0_3^-$** = 30 **$S0_4^{2-}$** = 60	1.250
LCS high **Cl^-** = 2.00 **$N0_3^-$** = 6.00 **$S0_4^{2-}$** = 12.0	31.250	**Cl^-** = 10 **$N0_3^-$** = 30 **$S0_4^{2-}$** = 60	6.250

Table 4. Target Concentrations for Cations in LCS Solutions

Final Conc. Na^+, K^+, & NH_4^+ (ppm)	Final Volume (mL)	LCS spiking Solution Concentration Na^+, K^+, NH_4^+ (ppm)	LCS spiking Solution Aliquot (mL)
LCS low 0.020	25.025	20	0.025
LCS med 0.276	25.350	20	0.350
LCS high 0.769	26.000	20	1.000

Method Blanks (MBs) are prepared during the extraction of samples. An empty 50 mL centrifuge tube is filled with the same volume of DI water used to extract filters using the autodilutor.

8.2 Sample Preparation

Filter Extraction Procedure (see **Figure 2** for an example of the extraction worksheet). Follow Section 8.2.1 when extracting ambient air filters. Follow 8.2.2 when extracting new Nylon batch filters. Note: A glove box under nitrogen (N_2) with magnesium oxide coated denuders placed inside will be used to extract new batches of nylon filters to reduce interferences from nitrous and nitric acid.

8.2.1 Extraction of Ambient Air Filters

- Label flat bottom tubes with moisture-resistant labels that have been pre-printed with the filter identification for the sample batch to be extracted. Carefully place the label near the top of the tube to prevent loss during the sonication procedure.
- Remove filters to be extracted from the freezer and allow them to equilibrate to room temperature.
- Put gloves on hands, rinse well with DI water, shake dry, and wipe away residual water with clean Kimwipe prior to handling tweezers or samples.
- Using tweezers, place each filter in a tube that has been labeled with the sample identification (ID). Note: Be sure that the label on the tube matches the label on the Petri dish.
- Transfer the tube containing the filter from the box into the sample racks used for the autodilution system.

- When the rack for the autodilution system is filled, remove the caps from the tubes and place them face up in order on a Kimwipe next to the SimPrep autodilutor.
- Following procedures from the analytical method for the autodilutor, add 25 mL of DI water to each centrifuge tube.
- Once tubes are filled, remove from the autodilutor and recap making sure to screw the caps on tightly. When extracting new batch Nylon filters, cap the vials tightly, place vials in sample racks that are used during ultrasonication.
- Place the sample racks containing the tubes in the ultrasonic bath and sonicate for 60 minutes.
- Remove the rack containing the tubes from the bath and place samples on shaker table for 8 hours. Shaker tables are used in cold storage room maintained at ~4°C. Sample will be maintained at ~4°C until analysis.

8.2.2 New Nylon Batch Filters

- New batches of nylon filters must be evaluated prior to use. The RTI Sample Handling and Receipt Laboratory (SHAL) will provide the IC lab with petri slides containing the new filters. The filters will be placed into refrigerated storage until extraction. For labelling of the extraction vial, carefully place the label near the top of the tube to prevent loss during the sonication procedure.
- Put gloves on hands, rinse well with DI water, shake dry, and wipe away residual water with clean Kimwipe prior to handling tweezers or samples.
- Rinse the tweezers using DI water, shake dry and blot away residual water with clean Kimwipe.
- Clean the inside of the working surfaces of the glove box with DI water and dry with a clean Kimwipe.
- Rinse the outside of the glove box gloves with DI water and dry with a clean Kimwipe.
- The glove box is stored in the basement in Johnson near the clean room, move the glove box into Johnson 187 bay 6.
- Connect the house N_2 to the glove box.
- Place two magnesium oxide coated denuders into the glove box.
- Place labeled extraction vials and DI rinsed clean dry tweezers in the glove box.

- Close all the glove box doors tightly and purge with N_2 for 30 minutes.
- Remove filters to be extracted from the refrigerator and allow them to equilibrate to room temperature inside of the entry chamber of the glove box for 30 minutes. Only open the interior door of the entry chamber after the main outer door has been closed tightly.
- Using tweezers, place each filter in a tube that has been labeled with the sample ID. Note: Be sure that the label on the tube matches the label on the Petri dish.
- Rinse disposable 50 mL beakers and fill them with DI water to be used for extracting filters into the entry chamber of the glove box.
- Place an empty disposable plastic 50 mL beaker into the glove box to use when rinsing the pipette tip.
- Place 25 mL pipettes and clean pipette tips into the entry chamber of the glove box. Close the outer door to the entry box tightly
- Move the supplies into the inner N_2 chamber.
- Rinse the pipette tip three times with DI water before use. The pipette tip can become contaminated if it touches the inside surface of the glove box, gloves, beakers etc. If the pipette touches anything it must be replaced with a clean tip and the clean tip must be rinsed three times before use.
- Prepare a method blank by pipetting 25 mL of DI water into an empty tube and cap tightly. Prepare a method blank after every 25 samples and at the end of the batch.
- Pipette 25 mL of DI water into tubes and cap the tubes tightly.
- Once tubes are filled, remove from the glove box.
- Place the sample racks containing the tubes in the ultrasonic bath and sonicate for 60 minutes.
- Remove the rack containing the tubes from the bath and place samples on shaker table for 8 hours. Shaker tables are used in cold storage room maintained at ~4°C. Sample will be maintained at ~4°C until analysis.
- Document the use of the glove box and extraction of filters in the glove box logbook maintained with the glove box.
- After analysis, excel data files will be sent to the SHAL for verification and confirmation of acceptability of new filters.

8.3 Calibration Standards

Preparation of intermediate standards (Intermediate Standard A and Intermediate Standard C) are stable for at least six (6) months.

A minimum of eight (8) calibration standards will be prepared directly from Intermediate Standard A for anions as shown in **Table 5**. A minimum of 6 calibration standards will be prepared directly from Intermediate Standard C for cations as shown in **Table 6**. These standards will either be used that day or refrigerated (for no more than sixty [60] days).

Anions 1000 ppm, NIST-traceable, commercial SO_4^{2-}, NO_3^-, and Cl^- and 1000 ppm, will be used to prepare the Intermediate Standard A. A 10.0 mL aliquot of the 1000 ppm SO_4^{2-}, NO_3^-, and a 2.0 mL aliquot of Cl^- will be diluted to one hundred (100) mL in DI water to prepare a 100 ppm (SO_4^{2-}, NO_3^-) and 20 ppm (Cl^-) Intermediate Standard A.

Table 5. Anions

Anions	Volume of Intermediate A added (mL)	Diluted Volume (mL)	Final Concentration SO_4^{2-}, NO_3^- (mg/L)	Final Concentration Cl^- (mg/L)
Level 1	0.100	200	0.05	0.010
Level 2	0.200	200	0.100	0.020
Level 3	0.200	100	0.200	0.040
Level 4	0.500	100	0.500	0.100
Level 5	2.00	200	1.00	0.200
Level 6	3.00	100	3.00	0.600
Level 7	20.0	200	10.0	2.00
Level 8	25.0	100	25.0	5.00

Cations 1000 ppm, NIST-traceable, commercial Na^+, K^+, and NH_4^+ will be used to prepare the Intermediate Standard C. A 10.0 mL aliquot of 1000 ppm Na^+, K^+, and NH_4^+ will be diluted to 100 mL in DI water to prepare the 100 pm Na^+, K^+, and NH_4^+ Intermediate Standard C.

Table 6. Cations

Cations	Volume of Intermediate C added (mL)	Diluted Volume (mL)	Final Concentration Na^+, K^+, NH_4^+ (mg/L)
Standard 1	0.010	100	0.010
Standard 2	0.050	100	0.050
Standard 3	0.100	100	0.100
Standard 4	0.200	100	0.200
Standard 5	0.300	100	0.300
Standard 6	0.500	100	0.500
Standard 7	1.000	100	1.000
Standard 8	3.000	100	3.000

8.4 Sample Storage

Extracts will remain refrigerated at ~4^{0}C for a minimum of 6 months following analysis.

9.0 ANALYSIS BY ION CHROMATOGRAPHY

The analyst will follow maintenance and operation procedures listed in the RTI SOP 203-EQP-008.4: *Operation and Maintenance of Dionex Ion Chromatography Systems*. The analysis will be set up to run a complete calibration curve at the beginning of the run. DI water blanks will be run prior to the calibration curve for sample loop rinsing. QC samples are analyzed at the beginning and end of the sample queue and after every ten samples to ensure instrument stability. Typically, 50 samples complete an analytical batch. Three duplicates and two matrix spikes (prepared by spiking 0.2 mL of a known concentration into 3 mL of sample when using AS40 autosamplers and 0.05 mL of a known concentration into 0.75 mL of sample when AS-AP autosamplers are used) are included with each batch of 50 samples. The Dionex Chromeleon® software is set up using quadratic functions for the calibration of all anions and cations except for ammonium which is a cubic fit function. Dionex recommends using a cubic function for the calibration of ammonium.

9.1 Calculations and Data Reduction

Peak areas are entered into the computer where calculations are performed using a quadratic fit to the calibration data.

The quadratic fit yields the following:

$$y = ax^2 + bx + c$$

Where:

y = the instrument response
x = the calculated anion concentration, µg/L
a = curvature
b = slope
c = offset

The cubic fit yields the following equation:

$$y = zx^3 + ax^2 + bx + c$$

Where:

y = the instrument response
x = the calculated anion concentration, µg/L
z = cubic coefficient
a = curvature
b = slope
c = offset

Initially, the calibration curve is used for the calculation of the extract's chloride, nitrate, sulfate, sodium, ammonium, and potassium. When measured concentrations of any ion exceeds the highest standards listed in **Tables 5 and 6**, an aliquot from the extract is diluted to bring the ion concentration into the calibration range.

LCS results are used to calculate uncertainty when data are measured for IHLAP samples. The uncertainty is calculated annually. For the samples reported to the Chemical Speciation Network, UC Davis calculates the measurement uncertainty as a part of their quality review process utilizing field and analytical factors that can affect uncertainty.

10.0 METHOD PERFORMANCE

10.1 Quality Control Samples

Upper and lower control limits for QC standards and matrix spikes are set at ± 10 percent (%) for ions with concentrations above 0.050 milligrams/liter (mg/L). When ion concentrations in the QC standards fall below 0.050 mg/L, the acceptable range is ± 35%. If a QC standard sample fails, a second QC sample may be analyzed to verify the calibration. If this sample fails, samples bracketed by the failed QC are reanalyzed.

The acceptance criterion for duplicates is based on the sample concentration. Near the detection limit, variability will increase and therefore limits are ± 200%. For sample concentrations greater than ten times the detection limit, acceptable ranges are ± 10%. For sample spikes, recoveries within 90 to 110% of target values are acceptable. When QC criteria fail for duplicates or matrix spikes, the sample impacted is reanalyzed as are 5% of the samples analyzed within the entire sample queue to verify precision and ascertain if more than one sample was impacted. If other samples reanalyzed fail to meet the duplicate criteria, the entire set is reanalyzed. The acceptance criteria for DI water blanks added at the start of the calibration must fall at or below 2 times the current MDL.

10.2 Linearity

The correlation coefficient of the calibration curve must be $\geq$ 0.999 when the instruments are calibrated up to calibration standard 7. When calibration standard 8 is used to calibrate for samples which exceed calibration standard 7 concentrations, the acceptable coefficient is $\geq$ 0.995.

11.0 CALCULATIONS

11.1 Details of Calculations for QC Samples

The expected recovery for QC samples is calculated for recovery by:

$$\%Recovery = \frac{Vspk - Vs}{Spk}\ x\ 100$$

Where:

V_{spk} = value observed of the spiked sample
V_s = value observed of the unspiked sample
S_{pk} = value of the spike.

Duplicate precision is calculated as the relative percent difference by:

$$RPD = \frac{(V - Vdup)}{(V + Vdup)/2}\ x\ 100$$

Where:

V = value of primary result
V_{dup} = value of duplicate result.

12.0 INSTRUMENT DETECTION LIMITS AND METHOD DETECTION LIMITS

12.1 Instrument Detection Limits

The Instrument Detection Limits (IDL) are calculated by measuring a DI blank sample 7-10 times by IC.

- Calculate the standard deviation of all the results.
- The IDL is calculated using students t (n-1) at a 99% confidence level.

12.2 Method Detection Limits

Method Detection Limit (MDL) is defined as the minimum concentration of an analyte that can be measured and reported with 99% confidence that the measured concentration is distinguishable from method blank results. The following steps are used to derive the MDL for this Chemical Speciation method on multiple instruments:

- Process seven spiked water samples and seven method blank water samples through all steps of the method. With multiple instruments, each instrument must analyze at least two samples and two blanks within the 12-month period.
- Existing data and blanks used for MDL calculation can be used if compliant with the requirements for at least three batches, analyzed on three separate days, and generated within the last twelve months.
- If blanks are collected throughout the year (e.g., batch method blanks), can be used to calculate the MDL Blank (MDLb). Do not use blanks derived from gross failures.
- If not using existing data, samples used for the MDL must be prepared in at least three batches on three separate calendar dates and analyzed on three separate calendar dates.
- Preparation and analysis may be on the same day for the batch.
- Prepare a spike of the target analyte 2 to 5 times greater than the expected MDL each sample.

- Analyze each sample.
- Calculate the standard deviation of the spiked samples.
- The student t-value used to calculate the MDL will represent the number of samples used by the laboratory, which is in accordance with 40 CFR Part 136.3, Appendix B, Revision 2.
- If none of the method blanks give numerical results for an individual analyte, the MDLb does not apply.
- If some (but not all) of the method blanks for an individual analyte give numerical results, set the MDLb equal to the highest method blank results. If more than 100 method blanks are available, set MDLb to the level that is no less than the 99th percentile of the method blank results. For "n" method blanks where n ≥ 100, sort the method blanks in rank order. The (n * 0.99) ranked method blank result (round to the nearest whole number) is the MDLb.
- If the calculated MDLb is higher than the calculated MDL spike for any element, then it is assumed there is blank contamination and corrective action must be taken to identify the source of the contamination. The MDL study must be re-done so that the MDLs is higher than the MDLb
- MDLs are determined annually, and corrective action will be taken if the detection limits do not meet the contract-required detection limits.

13.0 DATA MANAGEMENT

13.1 Data Processing

The chromatography data for all samples analyzed are reviewed twice before data are exported via Excel into a database file (see **Figures 3 and 4** for examples of the Level 0 and Level 1 worksheets). The reviewers ensure that all peaks are marked for the correct ion and are properly integrated. Occasionally, manual integration of a peak is required. The manual integration is verified by both reviewers before it is processed. The reviewers verify that all QC samples, spiked samples, and duplicated samples meet data quality objectives defined in section 10.1 and certify that the calibration criteria are met for each batch of samples (see **Figure 5** for the detailed steps in data processing).

Data are transferred electronically from the instrument using Microsoft Excel. Report templates for anions and cations are utilized within the Dionex Chromeleon® software. The templates are set to provide sample injection time and date, sample injection ID, and the amount of chloride, nitrate, and sulfate, sodium, ammonium, and potassium in units of µg/L. Two copies of the data are copied from the report template into an Excel file. One copy includes all results with calibration standards 1 – 7. A second copy of the data includes all results with calibration standards 1 – 8. The results with calibration standards 1 – 8 are only used for any ion that exceeds the concentration limit of calibration standard 7 and is less than the calibration standard 8. These Excel files are saved temporarily on a universal serial bus (USB) drive. The data are then copied from the USB drive and stored on a secured server.

A database file is prepared with all results from the appropriate standard curve. This file is imported into the Ion Lab Data Review Application. The database program allows for a review of each batch or sample individually and includes sample name, sample type, project, and extraction volume of the sample. The database includes entry points from the reviewer that can be edited during data review. These fields include sample flags and sample comments, or selections to exclude data. The database also enables the data reviewer to review a QA report which shows duplicate percent differences, spiked sample recoveries, and QC sample recoveries. A QC report for each analytical batch is printed and maintained with hard copy files of the analytical queues, the COC, the sample receipt form, extraction records, and a sample extraction log. The database converts the concentration for each ion from µg/L to ug/filter. After the data reviewer completes review of the dataset for an entire batch, the packet of data is passed to QA to review. The QA reviewer verifies that all notes listed on the queues and sample extraction log are noted in the database. They confirm that level 0 and level 1 reviews have been completed, all QC checks have met criteria, and reanalyzed samples have met data quality objectives. They also check 5% of the data concentrations in the original Excel file to ensure it matches the data listed in the database. They check to ensure that samples requiring the high standard have the appropriate reported results. They confirm all QC issues are addressed by the level 0 or level 1 reviewers. They also confirm all reported results for sample reanalysis and that the data packet is complete. The reviewed packet is transferred back to the data reviewer and data are exported in an Excel file and prepared for export for the client. To export data, the data reviewer imports the list of samples received from the client and selects the analysis dates for samples on the list. This file

is compared to the sample list provided on the COC from the client to verify that all samples listed on the COC have results entered. The datafile is saved in .csv format and sent to the client via email.

The lowest calibration standard is the minimum reporting limit (MRL) for all ions reported to the client. Data that fall below the MRL are reported as <MRL. To meet existing project and client reporting requirements, results may be reported below the MRL, but must be stated on the report *"those results that fall below the MRL are informational only and the laboratory cannot verify results that fall below the MRL."*

13.2 Data Storage

All raw data acquired by the instrument will be stored on the computer hard drive, along with the processed data. At the completion of the study, or at least quarterly, data will be transferred from the instrument hard drive to a secondary storage device.

14.0 CORRECTIVE ACTION

Corrective action can be initiated by any staff member working on the project when an event occurs that causes any deviation from the SOP, bench sheet, or approved work processes. Management affiliated with the project will review and approve all corrective actions. Corrective actions will be implemented through document revisions or staff training.

Corrective action is initiated whenever a program QC failure has been identified (e.g., either the control limits or contamination issues). Corrective action procedures generally consist of routine or non-routine corrective actions, which are each described in the following subsections.

14.1 Routine Corrective Actions

Routine failures include those involving the calibration curve, QC standards for calibration verification and continuing calibration verification, duplicate sample analyses (not prepared as duplicates since we can only extract the filter once) and matrix spiked sample recoveries. These failures are handled by the analyst and Laboratory Manager or QA Officer and may be corrected at the bench level. After completing the analysis, any issues are documented in the data review forms (e.g., Level 0 and 1), and then the Laboratory Manager submits the data package containing all sample and reanalysis analytical queues, Level 0 and 1 review sheets, QC reports, to the independent data reviewer to complete a final check of all data. If it's determined that an overlooked failure occurred,

the information is returned to the Laboratory Manager who works with the analyst to complete the appropriate action.

14.2 Non-Routine Corrective Actions

Non-routine failures include PE, CRMs, and audit samples. The QA Officer reviews the PE, CRMs, or audit sample results for possible discrepancies. If a failure occurs, then the QA Officer will submit the failure report via e-mail to the Laboratory Manager, who, in turn, will go back to the analytical run to determine which corrective action is appropriate. This information will be reported back to the QA Officer via e-mail for approval on the agreed upon corrective action.

15.0 PREVENTATIVE MAINTENANCE

Preventive maintenance of the ion chromatography instruments is vital to ensure long-term operation. Maintenance activities for the instruments is addressed in *RTI SOP 203-EQP-008: Operation and Maintenance of Dionex Ion Chromatography Systems*.

16.0 WASTE MANAGEMENT

Laboratories are urged to protect air, water, and land by minimizing releases from hood and bench operations, complying with any sewer and discharge permits and regulations, and by complying with all solid and hazardous waste regulation. More information about waste management is presented in *The Waste Management Manual for Laboratory Personnel*, which is available from the ACS.

17.0 REFERENCES

17.1 RTI SOP 100-EQP-020.5*: Gravimetric Calibration Verification and Maintenance of Liquid Dispensing Devices*

17.2 RTI SOP 100-EQP-007.7*: Refrigerator and Freezer Monitoring, Maintenance and Operation with Storage Condition Definitions*

17.3 RTI SOP 100-EQP-009.7*: Calibration of Temperature Measuring Devices*

17.4 RTI SOP 100-EQP-004.6*: Calibration, Use and Maintenance of Balances*

17.5 RTI SOP Ions3*: Filter Extraction via SimPRep Autodilution System*

17.6 RTI SOP 203-EQP-008.4*: Operation and Maintenance of Dionex Ion Chromatography Systems*

17.7 40 CFR Part 136, Appendix B*: Definition and Procedure for the Determination of the Method Detection Limit (Revision 2)*

Sample Receipt Form

RTI Project Number:_____ Date Received:_____

Number of Samples: _____

Description: _____

Sample Storage Location: Johnson 2nd Floor, Freezer #_____

Batch #:_____

Sample Condition:

____ All samples were received in good condition.

____ The following discrepancies were found (see attached sheet if necessary):

____ The following actions were taken to resolve the discrepancies see attached sheet if necessary):

_____

_____

Acknowledgment of Receipt	
Sample Custodian	Date

Figure 1. Example of the sample receipt form.

EXTRACTION WORKSHEET	RESEARCH TRIANGLE INSTITUTE POST OFFICE BOX 12194 RESEARCH TRIANGLE PARK, NC 27709-2194	EXTRACTION DATE:_____ SAMPLE SET #: _____ PROJECT: CSN

TITLE: Extraction of Nylon Filters in Deionized Water

Sample Numbers:_____

General Instructions

Initial and date each task as soon as it is completed; sign the bottom of the page when all entries have been completed and have reviewer sign bottom of page. Data entries should be performed using indelible, black-ink ballpoint pens. Be sure to record scientific observations and deviations from this procedure on this document.

Reagents	Supplier	Lot Number	Exp. Date
Deionized (DI) Water	Milli-Q IQ 7000	NA	Drawn daily
Na^+ (1000 ppm Stock Solution)	NSI Lab Solutions		
NH_4^+ (1000 ppm Stock Solution)	NSI Lab Solutions		
K^+ (1000 ppm Stock Solution)	NSI Lab Solutions		
LCS spiking solution: 20 ppm Na^+,NH_4^+,K^+	Calibration and QA Standards Logbook (Located Johnson, Lab 187) Date_____ Pg#_____	NA	
Cl^- (1000 ppm Stock Solution)	NSI Lab Solutions		
NO_3^- (1000 ppm Stock Solution)	NSI Lab Solutions		
NO_2^- (1000 ppm Stock Solution)	NSI Lab Solutions		
SO_4^{-2} (1000 ppm Stock Solution)	NSI Lab Solutions		
LCS spiking solution: 60 ppm - SO_4^{-2} 30 ppm - NO_3^- 20 ppm - NO_2^- 10 ppm - Cl^-	Calibration and QA Standards Logbook (Located Johnson, Lab 187) Date:_____ Pg#:_____	NA	

Comments:

1

Analyst Signature: _____ Date: _____ Reviewer Signature: _____ Date: _____

Filename: Extraction Worksheet_V7 052223

Figure 2. Example of the extraction worksheet (page 1 of 6).

EXTRACTION WORKSHEET	RESEARCH TRIANGLE INSTITUTE POST OFFICE BOX 12194 RESEARCH TRIANGLE PARK, NC 27709-2194	EXTRACTION DATE:_____ SAMPLE SET #: _____ PROJECT: CSN

Equipment	Manufacturer/Model	Serial Number or ID# / Location
Deionized (DI) Water System	Millipore / Milli-Q IQ 7000	/ Johnson, Lab 187
SimPrep AutoDilution System #1	Teledyne / SimPrep	0122138A560 / Johnson, Lab 187
SimPrep AutoDilution System #2	Teledyne / SimPrep	0122139A560 / Johnson, Lab 187
Sonicator/Water Bath #1	Bransonic / 8510R-MT	RPA11097783F / Johnson, Lab 187
Sonicator/Water Bath #2	Bransonic / 8800	BGQ032124780B / Johnson, Lab 187
Temperature Probe #1	Fisherbrand / Traceable	/ Johnson, Lab 187
Temperature Probe #2	Fisherbrand / Traceable	/ Johnson, Lab 187
Adjustable Volumetric Pipette		
Adjustable Volumetric Pipette		
Adjustable Volumetric Pipette		
50mL Plastic Digestion tubes	Mold Pro / MP-108PW	n/a
Freezer ACS216-FRZ	General Electric / FP21SXARWH	DS160520 / Johnson hallway
Refrigerator/Freezer #2	Kenmore / Goldspot	VS30260205 / Johnson hallway
Refrigerator #4	Frigidaire / FRU17B2JW19	WA95000736 / Johnson hallway
Refrigerator #6	Frigidaire / FRU17B2JW19	WA95000723 / Johnson, Lab 247
Refrigerator #7	Whirlpool / WRR56X18FW02	U84903152 / Johnson hallway
Refrigerator #8	Whirlpool / WRR56X18FW02	U85102798 / Johnson, Rm 246
Stainless Steel Tweezers	n/a	n/a

SAMPLE EXTRACTION PROCEDURE

- Remove the filter samples for extraction from the freezer:

  Freezer Location _____Freezer ID# _____

  Date/Time taken out of freezer - **Date:** _____ **Time:**_____

  ☐**Analyst/Date** _____/_____

- **LCS Spiking Solution Cation – (6-month expiration/store in refrigerator)** If needed, prepare the LCS Spiking Solution: Add the appropriate amount of each analyte into a 250 mL volumetric flask as indicated in Table 1 below. Add DI water to the 250 mL calibration line and shake the solution to mix.

Table 1 – Preparation of LCS Spiking Solution

Analyte	Volume of 1000 ppm stock to add (mL)	Final Volume (mL)	Final Concentration (ppm)
Na^+, NH_4^+, K^+	5.00	250 mL	20

☐YES – LCS spiking solution prepared (note Logbook page # and Lot Id of the solutions in the comments box on the next page.)

☐NO – LCS spiking solution not prepared – removed from refrigerator ID# _____

☐Analyst/Date _____/_____

2

Analyst Signature: _____ Date: _____ Reviewer Signature: _____ Date: _____

Filename: Extraction Worksheet_V7 052223

Figure 2. Example of the extraction worksheet (page 2 of 6).

EXTRACTION WORKSHEET	RESEARCH TRIANGLE INSTITUTE POST OFFICE BOX 12194 RESEARCH TRIANGLE PARK, NC 27709-2194	EXTRACTION DATE:_____ SAMPLE SET #: _____ PROJECT: CSN

- **LCS Spiking Solution Anion – (6-month expiration/store in refrigerator)** If needed, prepare the LCS Spiking Solution: Add the appropriate amount of each analyte into a 250 mL volumetric flask as indicated in Table 2 below. Add DI water to the 250 mL calibration line and shake the solution to mix.

Table 2 – Preparation of LCS Spiking Solution

Analyte	Volume of 1000 ppm stock to add (mL)	Final Volume (mL)	Final Concentration (ppm)
Chloride	2.50	250 mL	10
Nitrite	5.00	250 mL	20
Nitrate	7.50	250 mL	30
Sulfate	15.0	250 mL	60

□YES – LCS spiking solution prepared (note Logbook page # and Lot Id of the solutions in the comments box below)

□NO – LCS spiking solution not prepared – removed from refrigerator ID# _____

□Analyst/Date _____/_____

- Rinse gloved hands and stainless-steel tweezers with DI water and dry with a clean Kimwipe:

  □Analyst /Date _____/_____

- Transfer each filter into an appropriately labeled 50 mL plastic digestion tube and verify that the filter ID matches the tube ID. Arrange all samples, method blanks, and LCS samples in autosampler racks in the order as indicated on the "Sample Tracking and Extraction Log" document.

  □Analyst /Date _____/_____

- **Method Blanks** - Prepare an appropriate number of Method Blanks as indicated on the "Sample Tracking and Extraction Log" document based on the number of samples that will be extracted by labeling a 50 mL extraction tube as "Method Blank". These tubes do not contain a filter.

  Number of Method Blanks prepared: _____

  □Analyst /Date _____/_____

COMMENTS:

3

Analyst Signature: _____ Date: _____ Reviewer Signature: _____ Date: _____

Filename: Extraction Worksheet_V7 052223

Figure 2. Example of the extraction worksheet (page 3 of 6).

EXTRACTION WORKSHEET

RESEARCH TRIANGLE INSTITUTE
POST OFFICE BOX 12194
RESEARCH TRIANGLE PARK, NC 27709-2194

EXTRACTION DATE:_____
SAMPLE SET #: _____
PROJECT: CSN

- **Cation LOW, MED, and HIGH LCS dilutions** - Prepare an appropriate number of LCS samples for dilution as indicated on the "Nylon Filter Sample List and Analysis Location" document based on the number of samples that will be extracted by labeling 50 mL centrifuge tube as "LCS Low", "LCS Med", and "LCS High". Add the appropriate amount of LCS spiking solution to each tube as indicated in Table 3.

Table 3 - Preparation of Cation Laboratory Control Samples

Final Conc. (PPM)	Final Volume (mL)	No. of Samples for Dilution Prepared	LCS spiking Solution Aliquot (mL)	Analyst/Date
LCS low Na^+, NH_4^+, K^+ 0.020 ppm	25.025		0.025	_____/_____
LCS med Na^+,NH_4^+,K^+ 0.276 ppm	25.350		0.350	_____/_____
LCS high Na^+,NH_4^+,K^+ 0.769 ppm	26.0		1.0	_____/_____

- **Anion LOW, MED, and HIGH LCS dilutions** - Prepare an appropriate number of LCS samples for dilution as indicated on the "Nylon Filter Sample List and Analysis Location" document based on the number of samples that will be extracted by labeling 50 mL centrifuge tube as "LCS Low", "LCS Med", and "LCS High". Add the appropriate amount of LCS spiking solution to each tube as indicated in Table 4.

Table 4 - Preparation of Anion Laboratory Control Samples

Final Conc. (PPM)	Final Volume (mL)	No. of Samples for Dilution Prepared	LCS spiking Solution Aliquot (mL)	Analyst/Date
LCS low Cl^- = 0.196 NO_2^- = 0.392 NO_3^- = 0.588 SO_4^{2-} = 1.18	25.5		0.500	_____/_____
LCS med Cl^- = 0.476 NO_2^- = 0.95 NO_3^- = 1.43 SO_4^{2-} = 2.86	26.25		1.25	_____/_____
LCS high Cl^- = 2.00 NO_2^- = 4.00 NO_3^- = 6.00 SO_4^{2-} = 12.0	31.25		6.25	_____/_____

4

Analyst Signature: _____ Date: _____ Reviewer Signature: _____ Date: _____

Filename: Extraction Worksheet_V7 052223

Figure 2. Example of the extraction worksheet (page 4 of 6).

EXTRACTION WORKSHEET	RESEARCH TRIANGLE INSTITUTE POST OFFICE BOX 12194 RESEARCH TRIANGLE PARK, NC 27709-2194	EXTRACTION DATE:_____ SAMPLE SET #: _____ PROJECT: CSN

- Prior to beginning the extraction of each round (4 autosampler racks), fill the 2-liter plastic rinse bottle and the 2-liter reservoir bottle with DI water directly from the Milli-Q system. These are the bottles used with the SimPrep auto dilution system.

  Record resistivity reading each time the 2-liter plastic bottles are filled – **must be 18.2 MΩ** to proceed.

  Note: sample numbers are taken from the "Sample Tracking and Extraction Log" – column 3

  Set 1 Bottle: Resistivity (MΩ): _____, Sample Numbers_____ Analyst/Date_____/_____

  Set 2 Bottle: Resistivity (MΩ): _____, Sample Numbers_____ Analyst/Date_____/_____

  Set 3 Bottle: Resistivity (MΩ): _____, Sample Numbers_____ Analyst/Date_____/_____

  Set 4 Bottle: Resistivity (MΩ): _____, Sample Numbers_____ Analyst/Date_____/_____

- Before each set, purge the SimPrep auto dilution system with 10,000 uL of water at least 5 times using the system software.

  ☐**Analyst /Date** _____/_____ **1 2 3 4 5**

- Review the most recent 'Demonstration of Autodilutor Performance' worksheet for the SimPrep autodilutor being used and record below the "Corrected SimPrep Volume Setting" for 25,000 uL. This is the setting that will accurately deliver 25 mL of DI water. Program the SimPrep to deliver this volume, place uncapped tubes in order on SimPrep, and hit start.

  Volume setting (uL): _____

  ☐**Analyst /Date** _____/_____

- Verify that all tubes have been filled with 25 mL of DI water. Second analyst verification required.

  Set 1: ☐Analyst /Date _____/_____ ☐ Second Analyst /Date _____/_____

  Set 2: ☐Analyst /Date _____/_____ ☐ Second Analyst /Date _____/_____

  Set 3: ☐Analyst /Date _____/_____ ☐ Second Analyst /Date _____/_____

  Set 4: ☐Analyst /Date _____/_____ ☐ Second Analyst /Date _____/_____

COMMENTS:

5

Analyst Signature: _____ Date: _____ Reviewer Signature: _____ Date: _____

Filename: Extraction Worksheet_V7 052223

Figure 2. Example of the extraction worksheet (page 5 of 6).

EXTRACTION WORKSHEET	RESEARCH TRIANGLE INSTITUTE POST OFFICE BOX 12194 RESEARCH TRIANGLE PARK, NC 27709-2194	EXTRACTION DATE:_____ SAMPLE SET #: _____ PROJECT: CSN

- Tightly cap all tubes and place samples in a Sonicator/ice water bath. Sonicate the samples for 60 minutes. Begin sonication by adjusting the built-in timer to 60 minutes. During sonication, the water bath temperature **should not exceed 27°C**.

  Set 1: Sonicator#_____Pre- temp °C _____ Time samples in Sonicator: _____
  Post-temp °C_____ Time samples removed from Sonicator_____

  Set 2: Sonicator#_____Pre- temp °C _____ Time samples in Sonicator: _____
  Post-temp °C_____ Time samples removed from Sonicator_____

  Set 3: Sonicator#_____Pre- temp °C _____ Time samples in Sonicator: _____
  Post-temp °C_____ Time samples removed from Sonicator_____

  Set 4: Sonicator#_____Pre- temp °C _____ Time samples in Sonicator: _____
  Post-temp °C_____ Time samples removed from Sonicator_____

  ☐**Analyst/Date** _____/_____

- Place samples on Shaker table in outside refrigerator for 8 hours.

  ☐**Analyst/Date** _____/_____

- Place the LCS Spiking Solution in the Refrigerator – **ID#**_____

  ☐**Analyst/Date** _____/_____

- Place the samples in the refrigerator after removing from the shaker table

  Refrigerator Location _____**Refrigerator ID#** _____

  Date/Time samples were placed in the refrigerator - **Date:** _____**Time:**_____

  ☐**Analyst/Date** _____/_____

COMMENTS:

6

Analyst Signature: _____ Date: _____ Reviewer Signature: _____ Date: _____

Filename: Extraction Worksheet_V7 052223

Figure 2. Example of the extraction worksheet (page 6 of 6).

ION CHROMATOGRAPH LEVEL 0 REVIEW

Date: _____ Analyst: _____

System: _____ Batch #: _____

	Reading	Consistent w/previous? (yes/no)	Analyst Initials
Background Conductivity			
Pump Pressure			

Sample order	Analyst Initials
Double check Autosampler rack position	
After analysis check of Autosampler rack position & sample order	

	Yes/No	Analyst Initials
Are DI blanks clean? "Clean" is defined as ≤ MDL for each anion or cation.		
Are peaks identified correctly on chromatograms?		
All calibration curves acceptable (≥ 0.999 w/o std 8)?		
Duplicates ± 10% 10 x MDL Duplicates ±100% MDL-10x MDL Anion MDL's Cl = 0.006 NO2 = 0.010, NO3 = 0.008, SO4 = 0.011 Cation MDL's Na, NH4 & K = 0.006		
Spike recovery 90-110%		
QC Samples ± 10% standards > 0.050 ppm, ± 35% standards ≤ 0.050 ppm[1]		

Please use the comments box below to address issues pertaining to inconsistencies between previous pump pressure and background conductivity results and corrective action required to address QC criteria failures.

Figure 3. Example of the Ion Chromatograph level 0 worksheet (page 1 of 2).

Comments

[1]QC samples are defined as Quality Control samples labelled as QC-Med, QC-Low, QC-Med HI, QC-Med-HI and QC-High when conducting anion analysis and QC Low, QC Med, QC Med Hi and QC High when conducting cation analysis.

LCS low QC, LCS Low Anion, LCS Med QC, LCS Med Anion, LCS High QC, and LCS High Anion are extraction check solutions prepared during the extraction. LCS Low Cation, LCS Med Cation and LCS High Cation are extraction check solutions prepared during the extraction.

Extraction solutions are monitored for recoveries, but do not disqualify data for control purposes, data are compiled for QA reports for projects requesting the data.

QA25, QA50, and QA75 are prepared to mimic real field extracts at the 25th, 50th and 75th percentile concentrations. These are used to monitor IC performance and analyst daily performance and not for instrument control purposes.

Figure 3. Example of the Ion Chromatograph level 0 worksheet (page 2 of 2).

ION CHROMATOGRAPH LEVEL 1 REVIEW

Date: _____ Analyst: _____

System: _____ Batch #: _____

	Yes/No	Analyst Initials
Are DI blanks clean? "Clean" is defined as ≤ MDL ppb for each anion and cation.		
Are peaks identified correctly on chromatograms?		
All calibration curves acceptable (≥ 0.999 w/o std 8)?		
Duplicates ± 10% 10 x MDL Duplicates +- 100% MDL-10x MDL MDL Anions Cl = 0.006 NO2 = 0.010, NO3 = 0.008, SO4 = 0.011 MDL Cations = 0.005 for Na, NH4 and 0.006 for K		
Spike recovery 90-110%		
QC Samples ± 10% for standards > 0.050 ppm and +- 35% for standards ≤ 0.050 ppm[1]		
Comments entered from extraction record		
Comments entered from queue		
Results needing high standard in curve replaced		
Reanalysis results selected as non-report in the database		

[1]QC samples are defined as Quality Control samples labelled as QC-Med, QC-Low, QC-Med HI, QC-Med-HI and QC-High when conducting anion analysis and QC Low, QC Med, QC Med Hi and QC High when conducting cation analysis.

LCS low QC, LCS Low Anion, LCS Med QC, LCS Med Anion, LCS High QC, and LCS High Anion are extraction check solutions prepared during the extraction. LCS Low Cation, LCS Med Cation and LCS High Cation are extraction check solutions prepared during the extraction.

Extraction solutions are monitored for recoveries, but do not disqualify data for control purposes, data are compiled for QA reports for projects requesting the data.

QA25, QA50, and QA75 are prepared to mimic real field extracts at the 25th, 50th and 75th percentile concentrations. These are used to monitor IC performance and analyst daily performance and not for instrument control purposes.

Revision Number 2 Revised 4/11/2023

Figure 4. Example of the Ion Chromatograph level 1 worksheet (page 1 of 2).

Samples ID for Samples requiring Reanalysis	Reason for Reanalysis	Date and Batch of Reanalysis	Result Replaced or Result OK

Comments

Revision Number 2 Revised 4/11/2023

Figure 4. Example of the Ion Chromatograph level 1 worksheet (page 2 of 2).

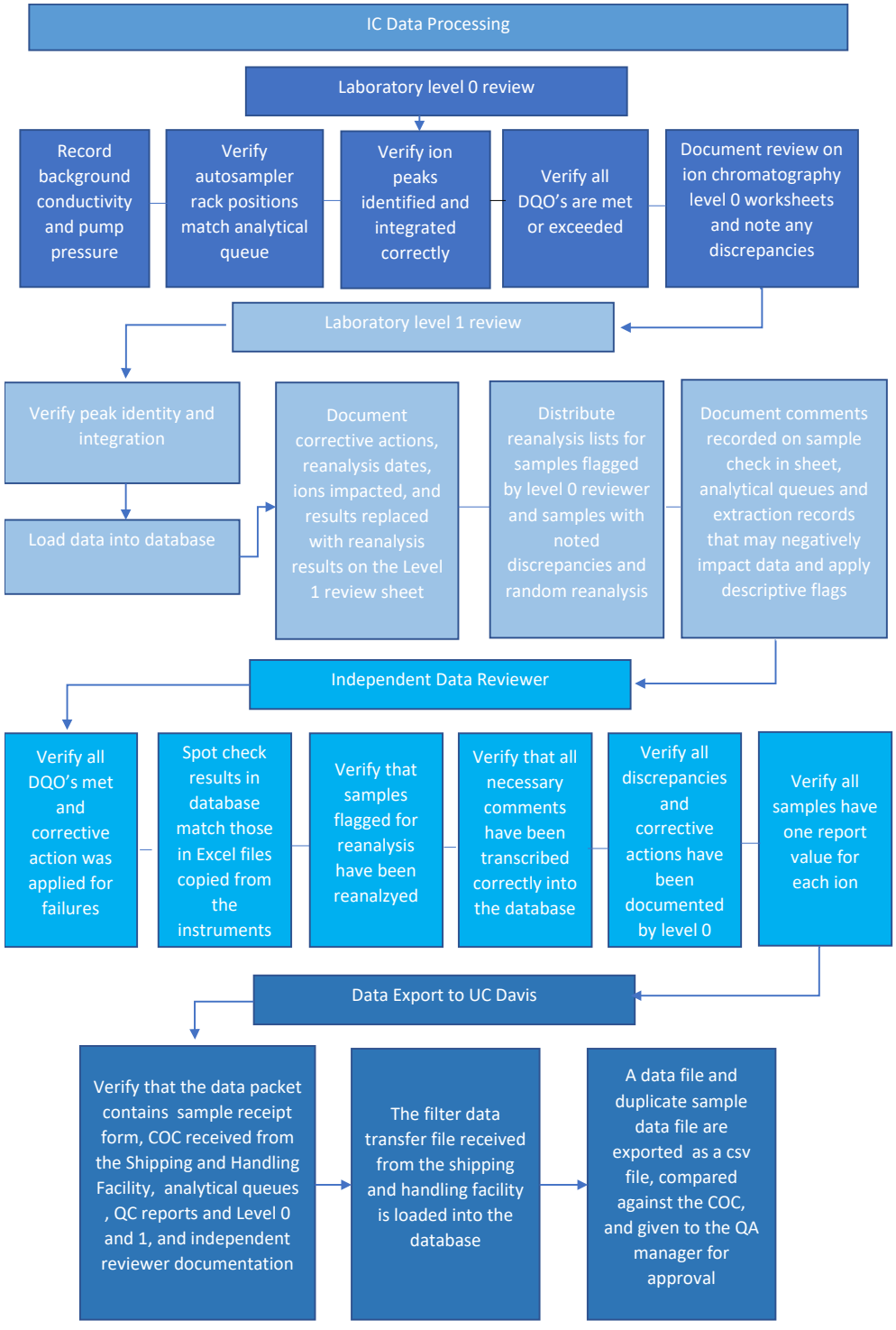

Figure 5. The data processing steps used to report ions concentrations.

REVIEW AND REVISION HISTORY

Version	Describe Major Changes or Indicate "Reviewed with No Revisions"	Effective Date/ Review Date	New Review Date
0	New SOP	01/23/2019	01/23/2020
1	Updated SOP to contain a definition section and a review and revision section and RTI SOP# assigned.	7/29/2019	7/29/2020
2	Updated SOP contain data review and processing section and complete yearly review	6/19/2020	6/25/2021
3	Annual review with minor editorial changes.	7/23/2021	7/23/2022
4	Modified data processing section to include flow chart, updated MDL procedure, minor editorial changes throughout the document.	2/16/2022	2/16/2023
5	Updated SOP to replace EasyPrep system with SimPrep system	7/11/2022	7/11/2023
6	Updated MDL procedure and SOP references; added in extraction procedure to prepare new Nylon filters for background evaluations, added in sections for maintenance and corrective action, and performed general edits and formatting	5/24/2023	5/24/2024
7	Updated SOP, edited section 13.1, and made general edits throughout the SOP.	4/12/2024	4/12/2025