

**TITLE: Acceptance Testing of Nylon Filters by Ion Chromatography
for the Chemical Speciation Network**

Effective Date: _____

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Table of Contents

1.0 Purpose..... 3

2.0 Scope 3

3.0 Summary of Method..... 3

 3.1 Method Interferences 3

 3.2 Deviations from the Method 3

4.0 Materials..... 4

 4.1 Apparatus..... 4

 4.2 Reagents..... 6

 4.2.1 Water and Single Compounds..... 6

 4.2.2 Anion Mixtures..... 7

 4.2.3 Cation Mixtures..... 8

5.0 Safety 10

6.0 Procedure 10

 6.1 Sample Extraction 10

 6.2 Sample Analysis..... 10

 6.3 Data Analysis 11

 6.4 Quality Control 11

 6.5 Calculations..... 12

 6.6 Corrective actions 12

7.0 References..... 12

8.0 Attachments 12

Figures

Figure 1. Overview – Laboratory Operations Procedures for Filter Acceptance Testing 5

Figure 2. Thermo/Dionex ICS-1600 Ion Chromatograph..... 6

Tables

Table 1. Anion Concentration Curves..... 8

Table 2. Anion CCV Concentrations 8

Table 3. Anion Blank Spike Concentrations 8

Table 4. Cation Concentration Curves (µg/mL)..... 9

Table 5. Cation Blank Spike Concentrations 9

1.0 Purpose

The purpose of this Standard Operating Procedure (SOP) is to provide consistent guidance to Wood Environment & Infrastructure Solutions, Inc. (Wood) personnel for the acceptance testing of nylon filters by ion chromatography (IC) in support of the Chemical Speciation Network (CSN).

2.0 Scope

The determination of selected anions and cations by IC on filters to be used for sampling by CSN.

- The anions of interest include: Chloride (Cl^-), Nitrate (NO_3^-), Sulfate (SO_4^{2+}).
- The cations of interest include: Sodium (Na^+), Ammonium (NH_4^+), Potassium (K^+).

3.0 Summary of Method

Filters from each box to be used for the project will be extracted and separate anion and cation analysis will be performed. An aliquot of the extract is injected onto columns containing ion exchange resins. The ions of interest are separated on the basis of their relative affinities for the exchange resin and their molecular weights. The separated ions are directed onto an electrolytic suppressor where the counter ions are removed from the eluent stream and only the highly conductive analytes remain in an aqueous mobile phase. Detection is by electrical conductivity. The resulting chromatographic peaks are identified on the basis of retention time compared to known standards. Quantitation is performed by comparison of peak area to the calibration curve areas. If the measured concentration for any of the analytes of interest exceeds 1 ug/filter, the corresponding box of filters will not be used for sampling.

3.1 Method Interferences

Interferences can be caused by substances with retention times that are similar to and overlap with those of the anions or cation(s) of interest. Column overloading can lead to peak tailing, poor peak resolution, and/or carryover into an adjacent downfield peak.

Method interferences may be caused by contaminants in the reagent water, reagents, glassware, or other sample processing accessories that lead to discrete artifacts or an elevated baseline in ion chromatograms.

Because the regenerant is chemically produced in the self-regenerating suppressor, changes in flow or electrical spikes may cause interfering peaks to appear in the sample chromatograms. These peaks are typically relatively small, asymmetrical, and extremely sharp. Broader, more rounded asymmetrical peaks may appear as a result of a change in operating conditions that is isolated to the suppressor itself.

3.2 Deviations from the Method

Deviations from the analytical method described in this SOP are not permitted.

4.0 Materials

4.1 Apparatus

- Analytical balance capable of accurately weighing to the nearest 0.01 gram (g)
- Ion chromatograph (2): Thermo/Dionex ICS-1600 (see Figure 1)
- Anion guard column: Thermo/Dionex AG14
- Anion analytical column: Thermo/Dionex AS14
- Anion self-regenerating suppressor: AERS 500
- Cation guard column: Thermo/Dionex CG16
- Cation analytical column: Thermo/Dionex, CS16
- Cation self-regenerating suppressor: CERS 500
- Conductivity cell detector: Approximately 1.25 microliter (μL)-internal volume or equivalent
- Appropriate autosampler vials and caps
- Eppendorf variable or fixed volume pipettors or equivalent with appropriate disposable tips
- Shaker tables
- Ultrasonic baths
- Class A volumetric flasks and pipets
- Nalgene bottles, 30 mL

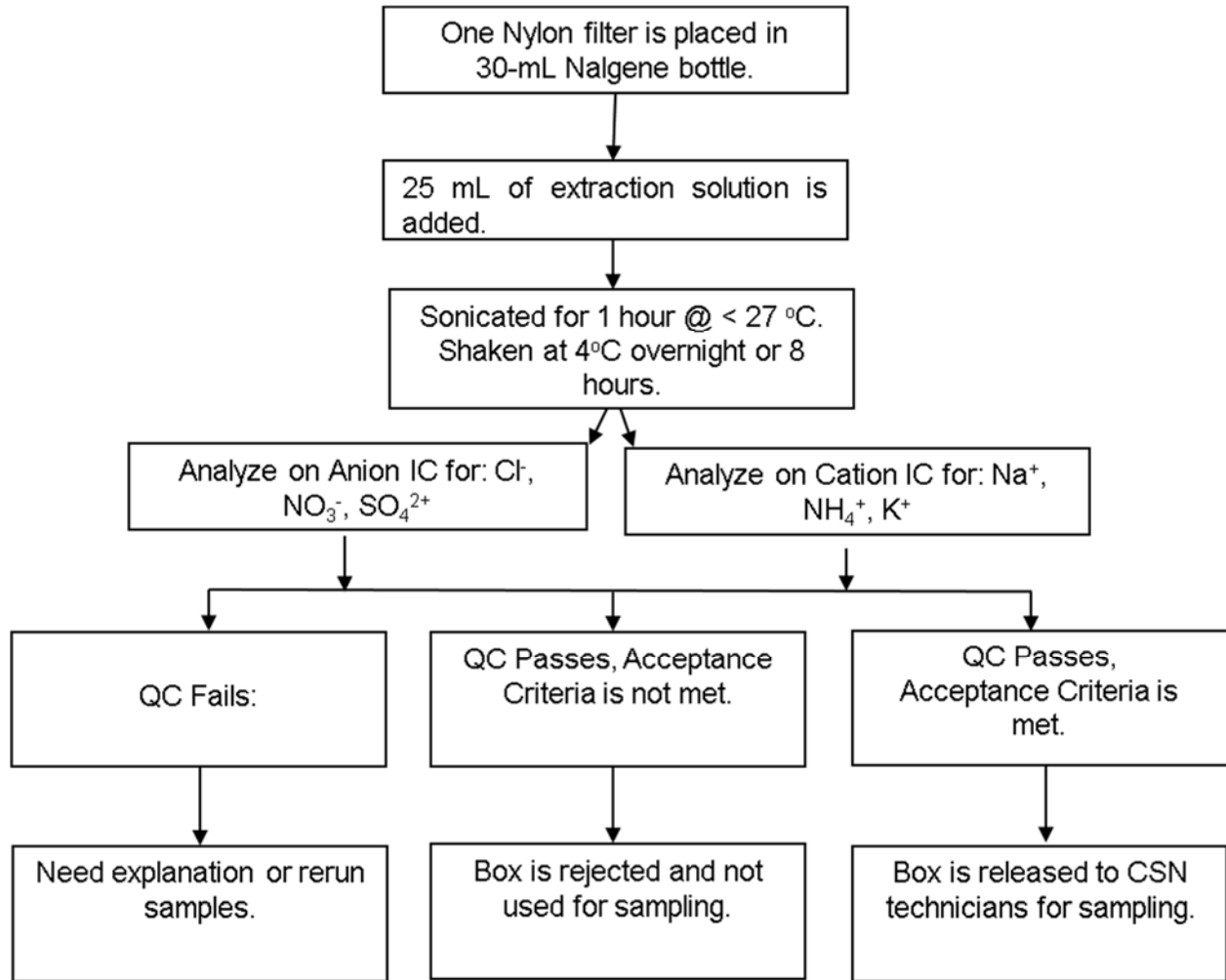


Figure 1. Overview – Laboratory Operations Procedures for Filter Acceptance Testing

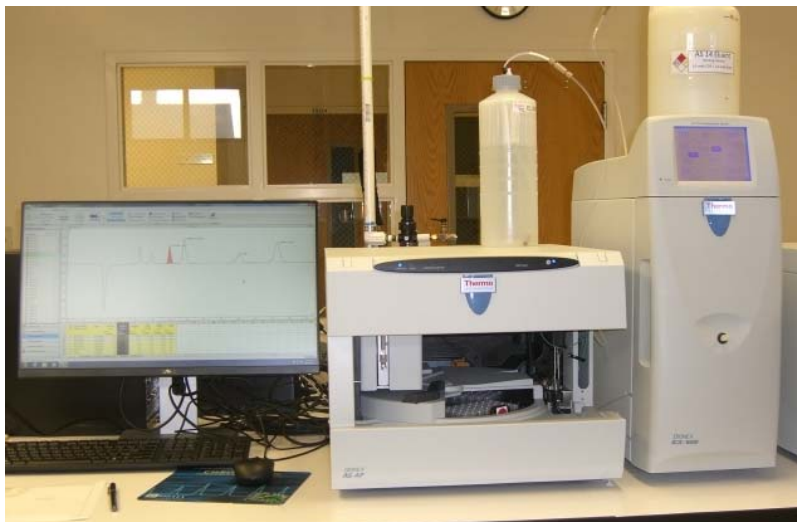


Figure 2. Thermo/Dionex ICS-1600 Ion Chromatograph

4.2 Reagents

4.2.1 Water and Single Compounds

- Reagent water: deionized (DI) water of resistivity of 15 mega ohms ($M\Omega$) or greater derived from mixed bed ion exchangers, activated carbon filters, and polishing exchangers. Water should contain particles no larger than $0.20\ \mu\text{m}$.
- Sodium bicarbonate (NaHCO_3), ACS reagent grade or better. CAS# 144-55-8
- Sodium carbonate (Na_2CO_3), ACS reagent grade or better. CAS# 497-19-8
- Methanesulfonic acid (MSA), >99%, ACS reagent grade or better. CAS# 75-75-2.
- Rubidium bromide, 1000 mg/L, dissolve 2.06 g of RbBr in a final volume of one liter (L) with DI. CAS# 7789-39-1.
- Individual Cation Calibration stock solutions ($1000\ \mu\text{g/mL}$) are purchased as National Institute of Standards and Technology (NIST)-traceable solutions. A Certificate of Analysis and an expiration date will be provided with each stock.
- Lithium stock solution ($100\ \mu\text{g/mL}$) is purchased as NIST-traceable solution. A Certificate of Analysis and an expiration date will be provided with each stock.
- Anion Mix Reference Standard containing Bromide, Chloride, Nitrate and Sulfate (100 ppm each) purchased from AccuStandard as a NIST-traceable solution. A Certificate of Analysis and an expiration date will be provided with each lot.
- Cation Mix Reference Standard containing Lithium, Ammonium, Potassium and Sodium (100 ppm each) purchased from AccuStandard as a NIST-traceable solution. A Certificate of Analysis and an expiration date will be provided with each lot.

- Extraction solution for nylon filters: To a 4-L glass bottle add approximately 2 L of DI water and 4 mL of the 1,000 mg/L Rubidium bromide stock. Bring to 4 L with DI water. The extraction solution must be tested prior to use and all analytes must be less than the reporting limits (see Attachment B).

4.2.2 Anion Mixtures

- Anion concentrated eluent for AS14 (100 mM NaHCO₃/350 mM Na₂CO₃):
Dissolve 16.78g NaHCO₃ and 73.96g Na₂CO₃ in DI and dilute to 2 L.
- Anion working eluent solutions (1.0 mM NaHCO₃/3.5 mM Na₂CO₃): Dilute 40 mL of the anion concentrated eluent solution to 4 L with DI.
- Anion Calibration stock solutions are purchased as NIST-traceable solutions. A Certificate of Analysis and an expiration date will be provided with each stock. These solutions are purchased as a set from AccuStandard. A minimum of five points shall be used for each calibration curve. The concentrations of the daily curve are listed in Table 1 in units of micrograms (µg) per mL.
- Anion Control standards used as continuing calibration verification (CCV) are purchased from High Purity Standards (HPS) as a NIST-traceable solution. The concentrations are listed in Table 2. A Certificate of Analysis and an expiration date is provided with each lot. A CCV is used to verify accuracy.
- Anion Standard Reference Material (SRM) intermediate solution (1.0 µg/mL) is prepared by diluting 1.0 mL of the 100 ppm Anion Mix Reference Standard to 100 mL with DI in a 100 mL Class A volumetric flask. The expiration date will be six months from the date of preparation.
- Anion SRM working solution (0.040 µg/mL) is prepared by diluting 10.0 mL of the 1.0 ppm Anion Mix Reference intermediate to 250 mL with DI in a 250 mL Class A volumetric flask. The expiration date will be one month from the date of preparation.
- Anion blank spike (BS) NIST-traceable solution purchased from High Purity Standards (HPS). A Certificate of Analysis and an expiration date is provided with each lot. The BS is used to verify the accuracy of the extraction. The final concentration of each analyte in the spiked solution is listed in Table 3.

Table 1. Anion Concentration Curves

Anion Standard (µ/mL)	Chloride (µ/mL)	Bromide (µg/mL)	Nitrate (µg/mL)	Sulfate
STD 1	0	1.0	0	0
STD 2	0.008	1.0	0.035	0.040
STD 3	0.020	1.0	0.089	0.10
STD 4	0.040	1.0	0.177	0.20
STD 5	0.10	1.0	0.443	0.50
STD 6	0.30	1.0	1.328	1.50
STD 7	0.60	1.0	2.656	3.0
STD 8	1.0	1.0	4.427	5.0

Table 2. Anion CCV Concentrations

Anion Standard	Chloride (µg/mL)	Bromide (µg/mL)	Nitrate (µg/mL)	Sulfate (µg/mL)
CCV	0.5	1.0	2.214	2.5

Table 3. Anion Blank Spike Concentrations

Anion Standard	Chloride (µg/mL)	Bromide (µg/mL)	Nitrate (µg/mL)	Sulfate (µg/mL)
Blank Spike	0.20	1.0	0.443	0.50

4.2.3 Cation Mixtures

- Cation concentrated eluent for CS16 (1.0 N MSA): Dissolve 48.05 g of 99% MSA in a final volume of 500 mL with DI.
- Cation working eluent solution (30mM MSA): Dilute 120 mL of 1.0 N MSA concentrate to 4.0 L with deionized water.
- 10 µg/mL intermediate cation calibration solution. 5 mLs of each 1000 µg/mL stock standard are added to a 500 mL volumetric flask and diluted to volume with DI. The intermediate solution will have an expiration date 6 months from preparation (or the expiration date of an individual stock if sooner).
- 100 µg/mL intermediate cation calibration solution. 20 mLs of each 1000 µg/mL stock standard are added to a 200 mL volumetric flask and diluted to volume with DI. The intermediate solution will have an expiration date 6 months from preparation (or the expiration date of an individual stock if sooner).
- The working curve will be prepared by adding the volumes listed in Table 4 to separate 500 mL volumetric flasks. The working curve will have an expiration date one month after preparation.

- A minimum of five points shall be used for each calibration curve. The concentrations of the daily curve are listed in Table 4 in units of micrograms (μg) per mL.
- Cation CCV (0.5 $\mu\text{g}/\text{mL}$ for each analyte) solution is prepared by diluting 5 mL of the 100 ppm Cation Mix Reference Standard to a 1000 mL final volume with DI in a 1L volumetric flask. The working CCV will have an expiration of 6 months from preparation (or the expiration date of an individual stock if sooner). A CCV is used to verify accuracy.
- Cation SRM intermediate solution (1.0 $\mu\text{g}/\text{mL}$) is prepared by diluting 1.0 mL of the 100 ppm Cation Mix Reference Standard to 100 mL with DI in a 100 mL Class A volumetric flask. The expiration date will be six months from the date of preparation.
- Cation SRM working solution (0.040 $\mu\text{g}/\text{mL}$) is prepared by diluting 10.0 mL of the 1.0 ppm Cation Mix Reference intermediate to 250 mL with DI in a 250 mL volumetric flask. The expiration date will be one month from the date of preparation.
- Cation BS NIST-traceable solution purchased from High Purity Standards (HPS). A Certificate of Analysis and an expiration date is provided with each lot. The BS is used to verify the accuracy of the extraction. The final concentration of each analyte in the spiked solution is listed in Table 5.

Table 4. Cation Concentration Curves ($\mu\text{g}/\text{mL}$)

Cation Standard	10 $\mu\text{g}/\text{mL}^1$	100 $\mu\text{g}/\text{mL}^1$	100 $\mu\text{g}/\text{mL}$ Li ¹	Li+ ²	Na+, NH ₄ +, K+ ²
STD 1			5.0	1.0	0.0
STD 2	1.0		5.0	1.0	0.02
STD 3	2.0		5.0	1.0	0.04
STD 4	5.0		5.0	1.0	0.10
STD 5	25.0		5.0	1.0	0.50
STD 6		5.0	5.0	1.0	1.0

Note: 1 = Volume of Intermediate Calibration Solutions (mL) diluted to 500 mL

2 = Working Curve Concentrations ($\mu\text{g}/\text{mL}$)

Table 5. Cation Blank Spike Concentrations

Anion Standard	Sodium ($\mu\text{g}/\text{mL}$)	Ammonium ($\mu\text{g}/\text{mL}$)	Potassium ($\mu\text{g}/\text{mL}$)
Blank Spike	0.10	0.258	0.10

Note: Acceptance criteria for quality control samples are listed in Section 6.4 and outlined in Attachment A.

5.0 Safety

The analyst must be aware of the hazards associated with the chemicals used in this method. Reducing the possibility of accidental absorption or ingestion minimizes the hazards. Eating and drinking are not permitted in areas where chemicals are used or stored. Laboratory coats, gloves, and safety glasses must be worn at all times when handling these chemicals. If the analyst is not familiar with the hazards associated with the chemicals being used, the Safety Data Sheets (SDS) must be consulted. The SDS by chemical and brand can be found in the Wood laboratory or at the [SDS/MSDS search web site at https://www.msdssearch.com/](https://www.msdssearch.com/) or the [Vermont Safety Information Resources, Inc. \(SIRI\) web site at http://www.hazard.com/msds/index.php](http://www.hazard.com/msds/index.php) using the CAS number.

6.0 Procedure

6.1 Sample Extraction

1. Calibrate the repipettor to 25 mL. The acceptable limits are 25.00 +/- 0.1 g. The repipettor is used to add extraction solution to all samples.
2. Randomly pull filters from each box to be used for the project and place in 30 mL Nalgene bottles. Two percent of all filters will be tested. For a box of 50 filters, one filter will be selected. For a box of 100 filters, two filters will be selected.
3. Prepare a method blank (BLK). The BLK is an empty, labeled bottle. BLK is extracted as a regular sample by adding 25 mL of the extraction solution using the repipettor.
4. One anion blank spike (BS) or laboratory control sample (LCS) is prepared by adding 25 mL of the extraction fluid to the bottle, removing 1 mL with a calibrated pipettor, and adding 1 mL of the stock anion BS solution using the calibrated pipettor with a fresh tip.
5. One cation blank spike (BS) or laboratory control sample (LCS) is prepared by adding 25 mL of the extraction fluid to the bottle, removing 1 mL with a calibrated pipettor, and adding 1 mL of the stock cation BS solution using the calibrated pipettor with a fresh tip.
6. 25 mL of extract solution is added to each sample bottle using the repipettor.
7. Extract the samples: 60 minutes sonication at 23-27°C (monitor the temperature and add ice to the sonicator to keep the temperature from exceeding 27°C), then shake for a minimum of 8 hours or overnight on a shaker table at 1 Hz and 4°C.

6.2 Sample Analysis

1. Establish a stable baseline by pumping the working eluent through the instrument for at least 30 minutes. The operator's manuals provided by the manufacturer contain detailed information regarding optimization of instrument performance and optimum operating criteria.
2. Load the auto-sampler vials beginning with the calibration curve followed by the extracted method blank (BLK1), the initial control standard (CCV1), the initial reference sample (SRM1), and extracted samples. Additional control standards

(CCV2 through CCV9, CCVA, and CCVB) should be run after every 10 samples and at the end of the analytical run. A second RF (SRM2) should also be run preceding the end-of-run CCVx.

3. Each auto-sampler vial cap is scored with a DI rinsed razor knife prior to being placed on the vial. This additional step prevents the auto-sampler needle from getting bent causing a bad injection/replacement.
4. Verify that the run-log printout auto-sampler positions are correct. the extract bottle IDs match the runlog and initial when complete.

6.3 Data Analysis

1. Data files are processed using algorithms contained in the data collection software. Chromeleon 7.2 from Thermo/Dionex is currently in use. Parameters are adjusted as dictated by instrument performance.
2. Examine all chromatograms visually. Note any anomalies in the data batch narrative.
3. Export the responses to an Excel spreadsheet.
4. Assemble the data batch folder, including copies of all extraction worksheets, run logs, certificates of analyses and processing methods, hard copies of each chromatogram, and any other necessary documentation.
5. If any analyte from an extracted filter exceeds 1 ug/filter, the box that the filter came from must be marked "Failed", removed from the lab and not used for sample collection.

6.4 Quality Control

1. One BLK is analyzed with each extraction. The BLK for extracted samples is the applicable volume of extraction solution followed by the appropriate extraction procedure. The BLK results must be less than two times the reporting limit for the analytes of concern as outlined in Attachment B.
2. A CCV is analyzed at a frequency of 10 percent for every analytical batch, as well as at the beginning and end of the run. The measured value of the CCV must be within ± 10 percent of the certified value.
3. A SRM is used for an initial and a final calibration verification. The measured value of the reference sample must be within ± 10 percent of the certified value.
4. Sample replicates (DUP1, DUP2, etc.) 5 percent of the samples are analyzed in duplicate (1 out of every 20). For samples greater than five times the reporting limit, the relative percent difference (RPD) of the replicate samples must be with ± 20 percent. For samples with concentrations less than or equal to five times the reporting limit, the absolute difference between sample and replicate must be less than the reporting limit.
5. All curves must contain a minimum of five points for quadratic calculations and have a correlation coefficient greater than or equal to 0.995.

6.5 Calculations

1. All calculations are performed with data reduction algorithms that reside in the instrument software.
2. Separate calibration curves are prepared for each ion of interest by plotting the response (peak area) of standards against concentration values using quadratic regression in the instrument software. Sample concentrations are calculated using the quadratic equation for the curve. The analyst may eliminate points to improve accuracy throughout the range of calibration but at least 5 points plus a blank must remain.

6.6 Corrective actions

Attachment A shows the corrective actions taken when the QC Samples are not within acceptance criteria.

7.0 References

Thermo/Dionex Corporation. 2009. ICS-1600 Ion Chromatography System Operator's Manual, Rev. 01, Document No. 065290. March 2009

U.S. Environmental Protection Agency (EPA). 2007. Guidance for the Preparation of Standard Operating Procedures, (SOPs) for Quality-Related Documents. EPA/600/B-07/001, April 2007.

8.0 Attachments

Attachment A – Corrective Actions

Attachment B – Filter Acceptance and Reporting Limits for Ions

Attachment A
Summary of Corrective Action Procedures for Ion Chromatography

Quality Control	Acceptance Criteria	Corrective Action
Calibration curve correlation coefficient	≥ 0.995	Rerun calibration standards. If still out of control, prepare new calibration standards and recalibrate the instrument, or document why data are acceptable.
Calibration curve responses	Brackets all samples	Dilute and reanalyze samples exceeding the calibration curve range, or document why data are acceptable.
Reference standard (SRM)	$\pm 10\%$ of the certified true value	Rerun standard. If still out of control, recalibrate instrument and reanalyze samples, or document why data are acceptable.
Control standard (CCV)	$\pm 10\%$ of the certified true value	Rerun standard. If still out of control, recalibrate instrument and reanalyze samples run since last acceptable CCV, or document why data are acceptable.
MB (BLK)	< 2 times the RL	Determine the cause of blank problem. Reanalyze the sample, if necessary, or document why data are acceptable.
Blank Spike (BS)	$\pm 20\%$ of target	Not established
Sample Replicate (DUP)	$\pm 20\%$ RPD if the sample is greater than 5 times the RL	Determine the cause of the problem. Reanalyze the sample, if necessary, or document why data are acceptable.

Notes: RL = Reporting limit (see Attachment B)
 RPD = Replicate percent difference

Source: Wood

Attachment B
Filter Acceptance and Reporting Limits for Ions

Analyte	Reporting Limit ($\mu\text{g}/\text{mL}$)	Reporting Limit ($\mu\text{g}/\text{filter}$)
Ammonium	0.040	1.0
Potassium	0.040	1.0
Nitrate	0.040	1.0
Sodium	0.040	1.0
Sulfate	0.040	1.0
Chloride	0.040	1.0