DETERMINATION OF SULFATE, NITRATE, CHLORIDE AND BROMIDE USING THE METROHM ION CHROMATOGRAPHY SYSTEM

TABLE OF CONTENTS

Page

1. SCOPE AND APPLICATION 2
2. SUMMARY OF THE METHOD 2
3. EQUIPMENT AND SUPPLIES 2
4. REAGENTS AND STANDARDS 4
5. SAMPLE PREPARATION PROCEDURE 7
6. SAMPLE ANALYSIS/QUANTITATION 8
7. MAINTENANCE 14
8. TROUBLESHOOTING 22
9. POST-RUN PROCEDURE 30
10. DATA ARCHIVAL 32
11. SAFETY/HAZARDOUS WASTE MANAGEMENT/POLLUTION PREVENTION 33
12. QUALITY CONTROL/DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES 33
13. REFERENCES/DEFINITIONS/VALIDATION DATA 36

APPENDIX OF SIGNIFICANT CHANGES 37

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

1. SCOPE AND APPLICATION

1.1. This method details the determination of sulfate, chloride, nitrate, and bromide in aqueous matrices (drinking, fresh and saline surface waters, effluents, influents) and solid matrices (soils, sediments). The calibration range is from the method detection limit (MDL) 0.20 to 120 mg Cl/L for chloride, 0.20 to 80 mg SO_4^{2-}/L for sulfate, 0.050 to 10 mg N/L for nitrate, and 0.016 to 1.0 mg Br/L for bromide. The range may be extended by dilution. The sulfate MDL for solid matrices is 6.0 mg SO_4^{2-}/kg.

1.2. The aqueous tests covered are W-SO4-IC(-F), W-CL-IC(-F), W-NO3-IC(-F), and W-BR-IC(-F).

1.3. For solid matrices, an aqueous extraction is performed (see DEP SOP NU-044) and the resulting extracts are analyzed. The solid tests covered by this SOP are S-SO4-IC, S-CL-IC, and S-NO3-IC.

2. SUMMARY OF THE METHOD

2.1. This method is based on EPA method 300.0, Rev. 2.1 (1993).

2.2. Anions are injected into the ion chromatograph and separated on an A Supp5-100 mm x 4.0 mm analytical column with Metrosep RP guard disc. A sodium carbonate/bicarbonate solution serves as a mobile phase.

2.3. Once separated, the anions pass through an anion suppressor where they are converted to their highly conductive acid forms and the sodium carbonate/bicarbonate eluent is converted to very weakly conductive water. The separated anions in their acid forms are measured by conductivity and are identified on the basis of retention times as compared to standards.

2.4. Ion chromatography eliminates the need to use hazardous reagents and it effectively distinguishes among the halides (Br^-, Cl^-, and F^-) and the oxy-anions (SO_3^-, SO_4^-, NO_2^-, and NO_3^-).

2.5. For a description of possible interferences, see 300.0, Rev. 2.1 (1993).

3. EQUIPMENT AND SUPPLIES

3.1. Metrohm Ion Chromatography System:

3.1.1. Metrohm 761 or 861 Compact Ion Chromatograph (including 853 Carbon Dioxide Suppressor)

3.1.2. Metrohm 788 or 838 IC Filtration Sample Processor

3.1.3. PC with IC Net (version 2.3 SR5 or greater) software and Microsoft Excel

3.1.4. Metrosep A Supp 5-100 Column (Metrohm USA P/N 6.1006.510). A spare column should be kept on hand.

3.1.5. Metrosep RP Guard Column (Metrohm USA P/N 6.1011.030)

3.2. Consumable parts used by the instrument which are either disposable after one use or frequently replaced:

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

3.2.1. Replacement RP guard discs (Metrohm USA P/N 6.1011.130)

3.2.2. 11 mL autosampler tubes with perforated caps

3.2.3. Metrohm 47 mm regenerated cellulose membrane filters, 0.15 μm pore size, and forceps to handle membranes

3.2.4. Replacement filters for inline filter cartridges (Metrohm USA P/N 6.2821.130)

3.2.5. Replacement carbon dioxide scrubber cartridges

3.2.6. Replacement PTFE tubing in 0.97 mm and 0.5 mm internal diameter sizes, and replacement PEEK tubing with 0.5 mm internal diameter

3.2.7. Replacement PEEK compression fittings, PVDF compression fitting, and PEEK barbed fittings

3.2.8. Peristaltic pump tubing:

3.2.8.1. Yellow-yellow for introducing sample into the ultra-filtration cell

3.2.8.2. Orange-orange for pumping sample filtrate into the sample loop

3.2.8.3. Yellow-orange to deliver regenerant to the suppressor

3.2.8.4. Orange-white to deliver rinse water to the suppressor

3.3. Glassware and pipets for preparing samples, spikes, reagents, and standards:

3.3.1. Class A volumetric glass pipets or properly calibrated Eppendorf micropipets with tips

3.3.2. Two 10 mL Class A graduated cylinders, calibrated to contain (TC), for measuring flow rates. A stopwatch is also useful for measuring flow rates.

3.3.3. Class A volumetric flasks and graduated cylinders for preparing reagents. Class A volumetric flasks are also used for preparing stocks and for diluting samples.

3.4. 10 mL disposable syringes and 25 mm syringe filters (0.45 μm pore size), for prefiltering samples

3.5. Tools for instrument maintenance (at least adjustable wrenches, hex keys, and a sharp probing tool)

3.6. Parafilm

3.7. A properly calibrated analytical balance, spatula, and weigh boats for weighing dry standards and reagents

3.8. Disposable polystyrene beakers to use in preparing dilutions or spikes

3.9. The following equipment is needed only if preparing eluent in the lab. It is not needed if bagged eluent is purchased for use:

3.9.1. 2 L filter funnel

3.9.2. Rubber stopper

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

3.9.3. Ultrasonic water bath

3.9.4. Glass wool

4. REAGENTS AND STANDARDS (SEE DEP SOPS NU-041 AND NU-042)

Note: Before preparing reagents or standards, or running samples, please read the safety notes in the safety/hazardous waste section of this SOP and the MSDS for the chemicals used in this analysis.

Note: Reagent and standard preparations must be documented in the Laboratory Information Management System (LIMS) 'Standard Preparation Tracker' module. Unique ID numbers for each standard and reagent are generated in the module and documented in the standard and reagent sheets submitted with each analysis folder. Certificates of Analysis for each purchased standard are maintained in a binder in C307. If available, a Certificate of Analysis for each purchased reagent is also maintained in the REAGENT_PREP folder. All containers holding standards or reagents must be labeled with their unique ID and expiration date.

Note: The volumes prepared for the reagents and standards may be altered by the analyst as necessary. The final concentrations of the constituents of a standard or reagent must not be changed.

4.1. Deionized (DI) water.

4.2. Bags of certified eluent can be purchased from Metrohm USA. Eluent can also be prepared in the lab if necessary, but it is preferable to use certified eluent.

4.2.1. M Pak A Supp 5 eluent (Metrohm USA P/N MPAK0050):

4.2.1.1. Unopened bags of certified eluent expire one year from the date received. The unopened bags of certified eluent must be marked with the date received.

4.2.1.2. Opened bags of certified eluent expire 30 days from the date opened. Upon being opened, label the bag with the date opened and the expiration date.

4.2.2. To prepare eluent in the lab:

4.2.2.1. Sodium Carbonate, Na_2CO_3

4.2.2.2. Sodium Bicarbonate, $NaHCO_3$

4.2.2.3. Soda Lime

4.2.2.4. Stock eluent - Dissolve 0.8400 g sodium bicarbonate and 3.3916 g of sodium carbonate in 700 mL DI water. Dilute to 1 L. Holding time is 14 days.

4.2.2.5. Working eluent - Dilute stock eluent by a factor of 10 with DI water. Place in filter flask and cap filter flask with rubber stopper. Connect the flask to a source of vacuum, and place it in an ultrasonic bath for 20 minutes before transferring it to the

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

eluent bottle. Pack the gooseneck of the carbon dioxide absorber assembly with glass wool and then fill the carbon dioxide absorber tube with soda lime. Do not re-use working eluent from an earlier run. It must be made fresh from the stock eluent for each run. The eluent bottle is not frequently used. If it has not been used in the past month, rinse it with acetone as described in section 7.7 before using. Rinse the eluent bottle at least three times with DI water before filling.

4.3. Suppressor Regenerant is a mix of sulfuric and oxalic acids, with a final strength of about 50 mM for each component:

4.3.1. Suppressor regenerant can be made by adding 60 mL of concentrated sulfuric acid and 126 g of ACS certified reagent grade oxalic acid dihydrate to DI water, and diluting to a final volume of 20 L. Holding time is 180 days.

4.3.2. Note that these instructions will produce regenerant of *approximately* 50 mM. Suppressor regenerant does not need to be prepared to exacting specifications.

4.4. Autosampler antibacterial rinsing solutions:

4.4.1. A 5 % methanol solution is used to rinse the autosampler after every injection. It is prepared by diluting 100 mL of HPLC or ACS grade methanol to 2 L with DI water. Holding time is 180 days.

4.4.2. 30 % hydrogen peroxide is used to prepare a solution to manually rinse the autosampler weekly. Hydrogen peroxide should be stored in an opaque bottle in the refrigerator. See manufacturer's information for expiration date.

4.4.3 A 10 mM oxalic acid solution is also used to rinse the autosampler weekly. It is prepared by adding 0.3152 g of ACS certified reagent grade oxalic acid dihydrate to DI water, and diluting to a final volume of 250 mL. Holding time,180 days.

4.5. Other solvents (HPLC or ACS grade) for cleaning:

4.5.1. Acetone is required for rinsing instrument reservoirs monthly.

4.5.2. Acetonitrile may be required for cleanup in the event of bacterial infestation.

4.6. Standards - Stock standards are prepared from ACS certified reagent grade materials, dried at 105 ºC for 24 hours. Holding time, 180 days. Store in refrigerator:

4.6.1. Stock Chloride, 10,000 mg Cl^-/L - Dissolve 21.0282 g potassium chloride in DI water and dilute to 1 L.

4.6.2. Stock Sulfate, 10,000 mg SO_4^{2-}/L - Dissolve 18.1402 g potassium sulfate in DI water and dilute to 1 L.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

4.6.3. Stock Nitrate, 1000 mg N/L - Dissolve 3.6091 g potassium nitrate in DI water and dilute to 500 mL.

4.6.4. Stock Bromide, 100 mg Br^-/L - Dissolve 0.1288 g sodium bromide in DI water and dilute to 1 L, or use a purchased certified Bromide standard (Ricca Chemical, cat# 1180-4, **1000 mg Br^-/L**).

Note: If using the 1000 mg Br^-/L purchased standard from Ricca, adjust volumes used to prepare working standards accordingly. See Table 1 below.

4.6.5. 100 ppm Working Standard for Bromide Spiking - Using a class A glass volumetric pipet or a calibrated Eppendorf micropipet, place 1 ml of 1000 ppm purchased certified standard from Ricca in volumetric flask partially filled with DI water and dilute to mark with DI water. Holding time, 30 days. Store in the refrigerator.

4.7. Combined Working Standards (Table 1) - Using a class A glass volumetric pipet or a calibrated Eppendorf micropipet, place appropriate volume of stock in a volumetric flask partially filled with DI water and dilute to mark with DI water. Holding time, 30 days. Store in the refrigerator.

Table 1.

	Amount Prepared	**Chloride**	**Sulfate**	**Nitrate**	**Bromide** (**Important:** check Stock solution information in 4.6.4 and 4.6.5)
L8	250 mL	120 ppm/3000 µL	100 ppm/2500 µL	10 ppm/2500 µL	1.0 ppm/2500 µL
L7	250 mL	40 ppm/1000 µL	70 ppm/1750 µL	4.0 ppm/1000 µL	0.60 ppm/1500 µL
L6	250 mL	10 ppm/250 µL	20 ppm/500 µL	2.0 ppm/500 µL	0.40 ppm/1000 µL
L5	250 mL	2.5 ppm/62.5 µL	10 ppm/250 µL	0.8 ppm/200 µL	0.20 ppm/500 µL
L4	250 mL	1.2 ppm/30 µL	5.0 ppm/125 µL	0.2 ppm/50 µL	0.10 ppm/250 µL
L3	250 mL	0.80 ppm/20 µL	1.0 ppm/25 µL	0.16 ppm/40 µL	0.060 ppm/150 µL
L2	250 mL	0.50 ppm/12.5 µL	0.5 ppm/12.5 µL	0.10 ppm/25 µL	0.040 ppm/100 µL
L1	250 mL	0.40 ppm/10 µL	0.2 ppm/5 µL	0.080 ppm/20 µL	0.030 ppm/75 µL
PQCK5 (PQL)	500 mL	0.50 ppm/25 µL	0.5 ppm/25 µL	0.10 ppm/50 µL	0.040 ppm/100 µL
MDL	250 mL	0.20 ppm/5 µL	0.2 ppm/5 µL	0.05 ppm/12.5 µL	0.016 ppm/40 µL
CHCK2 (CCV)	1000 mL	20 ppm/2000 µL	20 ppm/2000 µL	0.8 ppm/800 µL	0.20 ppm/200 µL
CHCK5 (CCV)	1000 mL	10 ppm/1000 µL	5.0 ppm/500 µL	0.8 ppm/800 µL	0.08 ppm/80 µL
CHCKHI3	250 mL	120 ppm/3000 µL	70 ppm/1750 µL	10 ppm/2500 µL	1.0 ppm/250 µL

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

4.8. Prepare the Interference Check Standard (INT_STD) in a 250 mL volumetric flask using the indicated amounts of stock standard (adjust volume needed for Bromide depending on the stock concentration, see 4.6.4.):

Table 2.

ANALYTES:

Chloride	2.5 ppm/62.5 µL
Nitrate	1.0 ppm/250 µL
Sulfate	2.5 ppm/62.5 µL
Bromide	0.10 ppm/25 µL

Add interferences to the Interference Check Standard in the amounts indicated in Table 3 and bring to volume:

Table 3.

INTERFERENCES:

F	100 ppm/2500 µL
NO_2	1000 ppm/250 µL
PO_4	1000 ppm/250 µL

Also prepare 250mL of the CHCK1 (CCV, continuing calibration verification) standard. This is identical to the Interference Check Standard, except that it only contains the analytes, not the interferences. Holding time, 30 days for both standards. Store in the refrigerator.

4.9. A certified quality control (ALTQC) sample prepared following the manufacturer's instructions. See the manufacturer's certificate for concentration and expiration date. Store in the refrigerator.

5. SAMPLE PREPARATION PROCEDURE (SEE DEP SOP NU-033)

5.1. All samples are stored on ice or at ≤ 6 °C (not frozen). Samples to be analyzed for bromide and/or chloride **only** do not require the above storage.

5.2. Samples should be analyzed for bromide, chloride or sulfate within 28 days of collection date. Samples should be analyzed for nitrate within 48 hours of collection. If samples are analyzed outside these hold times, results must be reported with the Q qualifier code.

5.3. Solid matrix samples first undergo an aqueous extraction procedure according to DEP SOP NU-044.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

5.4. Remove the samples from the refrigerator following the proper protocols to preserve the samples chain of custody. Allow the samples to come to room temperature before pouring them into the autosampler tubes.

5.5. Samples for the IC are pre-diluted based on conductivity. See section 6.3. for detailed instructions.

5.6. For each batch - Prepare one matrix spike for every 10 samples. One batch may contain up to 20 samples. Prepare either a duplicate sample, if the components are known to be above the practical quantitation limit (PQL/PQCK5), or one matrix spike in duplicate. The Stock Sulfate (4.6.2.), Stock Chloride (4.6.1.), Stock Nitrate (4.6.3.), and Stock Bromide (4.6.4.) solutions are used as spiking solutions. Add the appropriate amount of spiking solution (10 – 50 µL of spiking solution) into a 10 mL portion of a selected sample (see also section 12.5.). Prepare one laboratory fortified blank (LFB) following the same procedure substituting DI water for the sample. Spike codes, preparation and labeling instructions for spikes are included in every analysis folder. Effluents are batched separately. Make sure that an effluent sample is spiked to represent the batch.

6. SAMPLE ANALYSIS/QUANTITATION

6.1. Preparing the Instrument:

6.1.1. Ensure that both the instrument and the autosampler are powered on. If the instrument was not already turned on, do not use it for at least 30 minutes after powering it up. The conductivity cell is kept at a constant temperature, and the heater will require at least this long to come to temperature.

6.1.2. Turn on the computer and log into IC Net. Open any system file (see 6.2.7. for a list of system files) by selecting File>Open>System. In the menu of the system window, select Control>Connect to Workplace.

6.1.3. Start up the system by selecting Control>Startup Hardware (Measure Baseline) from the system window menu.

6.1.4. Once the hardware starts, two windows will appear. One is the watch window which displays the current system conductivity and pressure. The other is the method window which displays the baseline. Monitor the system while it equilibrates; this should take about 2 hours under normal circumstances.

6.1.5. While equilibrating the system, be sure to periodically step the suppressor. In the system window, double-click on the instrument icon. The instrument window will open; this contains a “Suppressor” field, which shows how long it has been since the suppressor was stepped, and contains a <Step> button to manually step it. Step the suppressor no more frequently than every 10-11 minutes, and at least once per hour. If the suppressor is stepped too often, it will not be regenerated properly (since it will not be exposed to the acid for long enough). If it is not stepped often

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

enough, the baseline will go off scale. When the suppressor is stepped, the baseline will dip sharply, and then return.

6.1.6. As soon as you have begun equilibrating the system, perform all of the weekly maintenance detailed in section 7.5.

6.2. Preparing a Sample Queue:

6.2.1. IC Net uses a sample queue file to tell the instrument what cups to inject in what order. To prepare a sample queue, open an existing queue file using File>Open>Sample Queue. This will open the sample queue window. In this window, save the file under a new name, using File>Save as. Give the new queue file a name based on the date; use the format yymmddic#.que, where # is the number of the instrument. If there will be more than one queue run that day, append a letter a-z after the instrument number.

6.2.2. To edit the queue, click the <Edit> button in the sample queue window. This opens the queue editor. In the queue editor, rows are shown in blue if they have not been injected and pink if they have. Injected rows cannot be edited. If you have just re-named an existing queue, it will likely be mostly pink. To make it editable, select all the rows, then select Edit>Reset. This will mark all of the rows as uninjected.

6.2.3. Beginning with the calibration curve, enter your run sequence in the "Ident" column. When preparing your run sequence, remember to include all appropriate QC samples, including matrix spikes, LFBs, and duplicates. See sections 11.1 through 11.5. Remember to also include dilution factors for diluted samples (see section 6.3.1.).

An example run sequence includes:

CAL STDs L1-L8 (4.7.)
BLK_carryover (DI water, 4.1.)
INT-STD (Interference check standard, 4.8.)
CHCK1 (4.8.)
MDL (4.7.)
PQCK5 (4.7.)
ALTQC (4.9.)
CHCKHI3 (4.7.)
CHCK5 (4.7.)
BLK (DI water, 4.1.)
Batched samples (20 max.), including an MBLK, an LFB**.** (For matrix spikes and spiking instructions see section 5.6.)
CHCK2 (4.7.)
BLK

6.2.4. The autosampler holds 148 vials, labeled in ascending numeric order. It is not necessary to run vials in consecutive, numeric order, but this is generally best. In the "Vial" column, enter values beginning at 1, and

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

incrementing to the end of your sequence (or to the maximum of 148). For convenience, the queue editor can automatically increment this column (use Edit>Increment).

6.2.5. The "Level" column indicates whether a given vial contains a calibrant. It is very important that this column be properly filled out in advance. In IC Net, it is impossible to mark or unmark an injection as a calibrant after it has been injected! For each of the calibration standards, enter the appropriate level (i.e., L1 is 1, L2 is 2, etc.). For everything else, enter 0. For convenience, the queue editor can automatically fill a column with 0 or any other value (use Edit>Propagate).

6.2.6. The queue editor has two comment fields that can be used for whatever comments you wish. These comments will be attached to the chromatogram file (and can be printed on a chromatogram report, if this is desired).

6.2.7. The "System" column tells the instrument and the autosampler what system file to use when injecting the sample and acquiring data. A number of system files are in use, depending on where in the queue the sample is injected.

6.2.7.1. NonSequence.smt tells the instrument to load the sample at the current vial (defined in the "Vial" column of the queue), inject it, and then rinse the needle. This system can be used anywhere in the queue. It is used when cups are injected out of consecutive order. If an analyst is confused about systems, he can simply fill the "System" column with NonSequence.smt. The only drawback to this is that it adds about 3-4 minutes to each sample's run time.

6.2.7.2. If a group of samples is being run from a number of vials in consecutive, numerical order, and there is only one injection from each, different system files can be used to speed up the operation. The first sample in the group uses the Begin.smt system. The last sample in the group uses the Stop.smt system. All of the samples in between use the Sequence.smt system. With these systems, a sample is loaded into the loop while the previous sample is separating on the column. When using these systems, remember - all of the samples must be in consecutive positions on the autosampler, and each can only be injected once.

6.2.7.3. Begin.smt is used as described in 6.3.7.2. It tells the instrument to load the sample in the current vial, inject it, and then rinse the needle. Then, it pauses to let the sample inject. After a few minutes, it loads the sample in the next vial. Note that Begin.smt (and the systems described below) defines the "next vial" as the current vial number plus one, not as the vial number in the next line of the queue!

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

6.2.7.4. Sequence.smt is used as described in 6.3.7.2. It tells the instrument to inject the sample currently loaded into the loop, and then rinse the needle. Then, it pauses to let the sample inject. After a few minutes, it loads the sample in the next vial. Note that if this system is used without being preceded by Begin.smt, then it will begin by injecting whatever is in the loop (likely rinse water) and the current sample will not be injected. If Sequence.smt is launched when the valve is already in the Inject position, it will cause the sample queue to crash!

6.2.7.5. Stop.smt is used as described in 6.3.7.2. It tells the instrument to inject the sample currently loaded into the loop, and then rinse the needle. Note that Stop.smt does *not* send a shutdown instruction to the instrument; it simply tells the queue not to inject the next vial while the current one is running. If the next line in the queue does not contain the systems NonSequence.smt or Begin.smt, they will inject nothing, because Stop.smt loads nothing into the loop.

6.2.7.6. Cup148.smt is a special case. It is used in place of Sequence.smt when the current vial is the last vial on the carousel, position 148, and the next vial is 1. Thus, they allow a sequence of consecutive cups to "wrap around" from the end and go back to 1 (e.g., Cup148.smt allows …146, 147, 148, 1, 2, … to be treated as if they were in consecutive, numerical order).

6.2.8. In order to run the queue, the queue editor must be closed; as long as the queue editor is open, the queue being edited is paused. The exit button (a green check mark) automatically saves changes and exits. If you need to exit without saving, use File>Exit.

6.2.9. The sample queue can be printed from the queue editor and used as a bench sheet. Because of the potential for software errors (see Section 8.9.) you should not print a queue while it is running. Make sure the queue is saved before printing. If you need to print a queue that is in progress, pause it first (by clicking the <Pause> button in the queue window).

6.3. Sample Preparation:

6.3.1. Samples for the IC are pre-diluted based on conductivity or salinity. Use Table 4 as a guide.

Table 4.

Conductivity (μS/cm)	Salinity (PPTh)	Dilution Factor
0-449	0-0.20	nil
450-999	0.21-0.40	2
1000-2999	0.41-2.0	10
3000-9999	2.1-4.3	20
10,000-14,999	4.4-8.6	40

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

Conductivity (µS/cm)	Salinity (PPTh)	Dilution Factor
15,000-19,999	8.7-10.7	50
20,000-29,999	10.8-21	100
30,000+	22-43	200

6.3.1.1. If field conductivity is not available, lab conductivity is provided by any autotitrator analysis, even if the W-COND test is not scheduled. Lacking that, an estimated conductivity may be taken using a portable conductivity meter.

6.3.1.2. Samples to be analyzed for nitrate only should not generally be diluted according to conductivity. If time before sample expiration permits, these samples should be screened at a 1:10 dilution factor to determine the most appropriate dilution factor.

6.3.1.3. Make all dilutions with DI water. Dilutions of 1:50 or greater should be made serially, or in Class A volumetric flasks. Lesser dilutions can be prepared in the autosampler tube.

6.3.2. Samples run on the Metrohm do not generally need to be pre-filtered. However, if a sample contains so much sediment that you fear it may clog the autosampler's filter cartridge, you can pre-filter it with a syringe filter. If the sediment in a sample appears to be red clay, it should be pre-filtered; red clay particles stuck in the filter cartridge can cause a loss of sulfate recovery. All soil extracts must be prefiltered. If a water sample is filtered, note this on the sample queue or bench sheet.

6.3.3. Tubes placed in the 838 autosampler (instrument #2) must be uncapped. This autosampler lacks a needle shield, and will jam if injections are made from capped tubes. If a sample needs to be mixed in the tube (e.g., a spike or dilution), the tube can be capped, inverted to mix, and then the cap removed. Tubes placed in the 788 autosampler (instrument #1) may be capped with perforated caps. This will prevent evaporation over long runs. It is not, however, strictly necessary.

6.3.4. Be very sure that all tubes placed in the autosampler are seated properly. An improperly seated tube will jam the autosampler and cause the instrument to crash.

6.4. Once the baseline is equilibrated, close the method window. Then, open an empty method window (without a baseline) by double-clicking the computer icon in the system window. Note that the computer and monitor in the system window are two separate icons. Create a directory to store the current run's data; select Method>Method Setup, then select the "Processing" tab. This tab contains a field called "Chromatogram directory," which indicates where the chromatograms will be stored. By clicking the <Browse> button, you can change this directory or create a new one. The directory should be a subdirectory in the ICNet\Data\ directory. It should be named for the date (using the format yymmddic#). Close

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

the empty method window – you will be automatically prompted to save this change to the method.

6.5. You may now start the instrument. First, ensure that the suppressor was last stepped at least 10 minutes ago. Then, simply click the <Start> button in the queue window.

6.6. Running over multiple days:

6.6.1. The IC is capable of running over multiple days, as long as it does not run out of eluent, regenerant, or rinse. These bottles can be easily re-filled while the run is in progress. If a new eluent bag is needed, briefly pause the IC pump while changing bags (this should only take a few seconds), then ensure that the baseline is stable before re-starting. Re-equilibration of the baseline will likely take more than an hour so be sure to run a CCV and CCB (continuing calibration blank or BLK) before changing bags.

6.6.2. If running over multiple days, perform all of the daily maintenance indicated in 7.6 at the beginning of every day.

6.6.3. When running over multiple days, remember to run the PQL standard every 24 hours (see 12.6.). If it fails, shut down the run and begin again with a new calibration curve.

6.6.4. Whenever an injection has not been made for an hour or more, or whenever the pump stops (such as when replacing the eluent bag), run the QC indicated in section 12.7. before proceeding with new injections.

6.6.5. If a run requires more cups than the maximum capacity of the autosampler, simply begin again at position 1 on the autosampler – replace the injected cups with new cups.

6.6.6. A single sample queue can contain a maximum of 200 rows. To run more samples than this, simply use two sample queues – start one when the other finishes.

6.7. Shutdown:

6.7.1. The Metrohm can be set to automatically power down at the end of a sample queue. There is a check box in the queue window that turns this setting off or on. It is best to verify that an automatic shutdown works before too much time has elapsed, however. If a Windows error crashes or locks the computer, the instrument will never receive a shutdown signal. If it runs out of eluent (or, to a lesser degree, regenerant or rinse), it could be damaged.

6.7.2. To shut down manually, select Control>Shutdown Hardware from the menu in the system window.

6.7.3. After the instrument has shut down, select Control>Disconnect from workplace from the menu in the system window. Then exit ICNet and shut down the computer.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

6.7.4. After shutdown, unclamp the peristaltic pump tubing on the suppressor pump. This prolongs the life of the tubing. It is less important to take this step with the pump tubing on the autosampler, because it is replaced weekly, but, if you expect to reuse that tubing, unclamp it as well.

6.8. Quantitation/Calculations:

6.8.1. The instrument will give analysis results for:

Sulfate in mg SO_4^{2-}/L.

Chloride in mg Cl^-/L.

Nitrate in mg N/L.

Bromide in mg Br^-/L.

6.8.2. The QC Manager calculates recoveries for spikes and QC standards as well as relative percent differences (RPD) for duplicate samples and spikes. For general calculations including RPDs and spike recoveries, see section 5.9. of the FDEP Bureau of Laboratories Quality Manual.

6.8.3. The individual calibration standards are prepared according to section 4.7. The calibration is calculated by the instrument software for each component and is included in the analysis report. It also includes a correlation coefficient to evaluate the fit. The fit is third order.

7. MAINTENANCE

Note: All maintenance must be recorded in the instrument maintenance manual.

7.1. Keep the instrument clean and free of dust as much as possible. If eluent or sample is spilled, be sure to clean it up right away.

7.2. If any part of the flow path upstream of the column is to be disconnected, first disconnect the analytical column from the tubing connecting it to the suppressor. Otherwise, the column packing may shift, damaging or destroying the column.

7.3. When making connections, it is best to make flowing connections. That is, turn the pump on, and make sure the components being connected are filled with liquid, not air, before connecting them. This prevents air bubbles and voids from being introduced to the instrument.

7.4. Priming the pump:

7.4.1. The pump may not require priming before use if you are using bagged eluent. Prime the pump when using eluent made in the lab, when switching from the eluent bottle to a bag, or whenever the instrument has sat unused for an extended period.

7.4.2. Before priming the pump, be sure that the eluent source is connected to the high pressure-pump.

7.4.3. Open the purge valve.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

7.4.4. Insert a luer-tipped syringe into the connection on the front of the instrument.

7.4.5. Connect the software to the system if you have not already done so. See section 6.1.2.

7.4.6. In the system window, double click the instrument icon, opening the instrument window. In the "Flow" field, enter 2 mL/min. Click the <Send to Unit> button.

7.4.7. Click the <On> button in the "IC Pump" field to start the IC pump.

7.4.8. Using the syringe, draw the eluent through until no more air bubbles appear.

7.4.9. When the pump is primed, turn the IC pump off. Close the purge valve and remove the syringe. Set the flow rate of the pump back to 0.7 mL/min (remember to click the <Send to Unit> button).

7.5. Weekly maintenance. Perform the following maintenance procedures before you calibrate the instrument for the first time in a calendar week:

7.5.1. Make sure that the system is connected to a source of fresh eluent.

7.5.1.1. If using certified, bagged eluent, ensure that there is a bag on the stand, that it is within hold time, and that it contains sufficient eluent for the run you are planning. The tubing connecting the bag to the instrument attaches to the bag with a special fitting. It attaches to the inlet on the pump with a screw fitting that is screwed on by hand.

7.5.1.2. If using eluent made in the lab, prepare it and put it in the eluent bottle as described in section 4.2.2.5. The eluent bottle attaches to the inlet on the pump with an aspirating tube that slides directly onto the aspirating capillary on the pump. There is no fitting.

7.5.2. Ensure that the glass regenerant bottle on top of the instrument is filled with suppressor regenerant. Dump the contents of the glass rinse bottle on top of the instrument, rinse at least three times with DI water, then refill and replace. Check to ensure that the peristaltic pump tubing for the regenerant and rinse solutions is in good shape (not flattened or cloudy), and replace if necessary (see 7.8.2). Tighten the peristaltic pump clips if they were loosened at the end of the previous run.

7.5.3. Change the RP guard disc and supporting filter:

7.5.3.1. Remove the housing for the RP guard disc from the instrument.

7.5.3.2. The housing consists of two pieces, a screw fitting (called the "guard screw") and a sleeve (the "guard sleeve"). Open the housing using two wrenches.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

7.5.3.3. The old RP guard disc should now be easily removable by hand. There is also a supporting filter which will likely be attached tightly to the guard screw. You can remove it using a pointed tool.

7.5.3.4. Hold the guard screw vertically. Place a new supporting filter onto it. Place a new RP guard disc on top of the supporting filter.

7.5.3.5. While continuing to hold the guard screw in a vertical position, screw the guard sleeve on it from above.

7.5.3.6. Hand tighten the guard sleeve and then tighten an additional quarter turn with two wrenches. Do not overtighten or the guard screw could be damaged!

7.5.3.7. When replacing the housing on the instrument, be sure that it is not on backwards! The direction of flow is marked on the outside of the housing with an arrow; make sure this arrow points the same direction as the eluent flow. If the RP guard disc cartridge is put on backwards, the column may be damaged or destroyed.

7.5.4. Check the flow rate of the suppressor regenerant and rinse:

7.5.4.1. Downstream of suppressor, the suppressor regenerant and rinse flow into the waste line. These lines can be found at the rear of the instrument. The flow rates can be checked here, using a 10 mL graduated cylinder and a stopwatch. If the lines are not labeled, they can be distinguished by checking the pH of the liquid flowing out with pH paper (the regenerant is acidic).

7.5.4.2. The flow rate of the suppressor regenerant should be approximately 0.4-0.5 mL/minute. The flow rate of the suppressor rinse should be approximately 0.5-0.7 mL/minute.

7.5.4.3. If flow rates are not correct, you may need to change one or both pieces of peristaltic pump tubing (See 7.8.2.) or inline filters (See 7.8.1.).

7.5.5. Check the 853 CO_2 Suppressor absorber cartridge:

7.5.5.1. For more information, see sections 4.4.3. and 4.4.4. of the manual (see the reference in section 13.3.).

7.5.6. After the pump has been running for at least 30 minutes with the new RP guard disc and the instrument in operating configuration, note the pressure. If the pressure is abnormally high or low, see 8.1.

7.5.7. Clean autosampler probe, injection valve, and sample loop:

7.5.7.1. Weekly, two cleaning solutions are injected through the autosampler probe, injection valve, and sample loop, but not the

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

ultrafiltration cell or instrument flow path, to remove iron deposits and bacteria from the previous week's injections.

7.5.7.2. Fill two autosampler tubes with DI water.

7.5.7.3. In a third autosampler tube, place the10 mM oxalic acid solution (See 4.4.3.). It is a cleaning solution to remove iron and other metals.

7.5.7.4. In a fourth autosampler tube, prepare a 3 % hydrogen peroxide solution. This is a 1:10 dilution of 30 % hydrogen peroxide (See 4.4.2.), and can be prepared directly in the tube (1 mL of 30 % hydrogen peroxide to 10 mL in DI water). It is a cleaning solution to remove bacteria.

7.5.7.5. Disconnect the tubing that leads from the yellow-yellow pump tubing to the ultrafiltration cell where it connects to the ultrafiltration cell. Disconnect the inlet tubing from the autosampler to the instrument (which normally connects to the outlet of the orange-orange peristaltic pump tubing). Connect them together, so that the yellow-yellow pump tubing will pump the outlet from the probe directly into the instrument, bypassing the filtration cell.

7.5.7.6. Ensure that the injection valve is in the "Fill" position. Look at the instrument icon in the system window. At the bottom of the icon are buttons labeled "Inject" and "Fill." If the "Fill" button is greyed out, the valve is in the correct position. If not, click the "Fill" button.

7.5.7.7. Place the four autosampler tubes in four consecutive positions on the autosampler, in the order oxalic acid, DI water, hydrogen peroxide, DI water. You will inject them in this order.

7.5.7.8. In the future, a system file may be developed to automate the injection of these four cleaning solutions. Otherwise, inject them manually, using these steps:

7.5.7.8.1. In the IC Net system window, double-click on the autosampler icon. This will open the autosampler window. In this window, select the "Manual" tab, and then the "Manual" sub-tab. In the section labeled "Move," use the drop-down menu to select the position number of the vial you will be injecting, then click the <Start> button.

7.5.7.8.2. Below the "Move" section in the autosampler window is a section labeled "Lift." Using this section, you can lower the needle into the vial (IC Net uses the term "lift" for any vertical movement of the needle, whether up or down.). Select the "Work" position from the drop-down menu, then click the <Start> button. Once the needle is

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

in the rinse bottle, turn on the peristaltic pump, using the "Pump" section that is below the "Lift" section. Change "On," to "200" (seconds), then click the <Start> button.

7.5.7.8.3. When the pump is finished running, raise the needle by selecting "Shift" in the "Lift" section.

7.5.7.8.4. Repeat steps 7.5.7.8.1. through 7.5.7.8.3. for each of the four vials of cleaning solution, in order.

7.5.8. Change filtration membrane and pump tubing, and check flow rate:

7.5.8.1. Change the peristaltic pump tubing on the autosampler. There are two lines on the peristaltic pump. One uses yellow-yellow tubing to introduce sample into the filtration cell, the other uses orange-orange tubing to introduce filtrate to the sample loop. Cut peristaltic pump tubing in half between the anchors before placing it onto the instrument. There should only be one anchor on the tubing in use (on the upstream side). Do not tighten the tubing clamps yet (see 7.5.8.6.).

7.5.8.2. Change the filter in the autosampler's filtration cell. The filtration cell opens by removing five bolts. While the cell is open, wipe the grooves on both sides with a Kimwipe dampened with methanol, then rinse well with DI water. Put the new filter into place with forceps; be careful not to touch it with your fingers. Saturate the new filter with DI water and let it sit on the open cell, soaking, for 60 seconds. Then ensure that it is totally saturated with water before re-assembling and replacing the filtration cell.

7.5.8.3. Dump both DI water rinse bottles on the autosampler (i.e., bottles #2 and #3. If you are using an autosampler carousel with only two rinse bottles, there is only one DI water rinse bottle, #2). To remove the bottles, you may need to move the autosampler's carousel (see 7.5.7.8.1, and select any position away from the rinse bottles). Once the carousel has moved, you can remove the rinse bottles. Rinse them at least three times and fill them with DI water.

7.5.8.4. The other rinse bottle (i.e., bottle #1) is an antibacterial rinse of 5 % methanol (See 4.4.1.). Refill it.

7.5.8.5. Rinse the autosampler needle and filtration assembly. Move the autosampler's carousel to any DI water rinse bottle, using the same procedure as in 7.5.7.8.1. The rinse bottles are in positions beginning with "spec" or "Rinse," depending on the carousel used on the autosampler. In the "Lift" section, select "Rinse" instead of "Work." In the "Pump" section, select "On" instead of entering a specific number of seconds.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

7.5.8.6. Tighten the tubing clamps one click at a time until you see consistent flow. Do not overtighten them. When you are done, you can stop the pump by selecting "Off" in the "Pump" section of the autosampler window.

7.5.8.7. Rinse the needle and filter for five minutes. You can set a time by changing "On" to "300" (seconds) in the "Pump" section of the autosampler window, then clicking <Start>. During this time, observe the filter to ensure that sample is passing through it and into the loop, and that there are no trapped air bubbles.

7.5.8.8. Measure the flow rate to ensure that the ultra-filtration cell is set up correctly. There are two pieces of tubing that leave the ultra filtration cell. One is for waste and can be put directly into a TC graduated cylinder. The other goes to the instrument; this can be put into a graduated cylinder after it leaves the 6-port valve. Measure the flow rate for 180 seconds. The tubing coming from the instrument should produce at least 3.1 mL in this time. The waste tubing should produce significantly more than this (approximately 4.5 mL or more).

7.5.8.9. Raise the needle by selecting "Shift" in the "Lift section.

7.5.8.10. Carefully examine the two pieces of outlet tubing and all other tubing on the autosampler. If any tubing is becoming dark, it may have bacteria, algae, or mineral deposits within, change this tubing at once. Also inspect the sample probe for discoloration. Discoloration could indicate that the probe is contaminated with bacteria or sediments, and needs to be replaced if it cannot be cleaned.

7.6. Daily maintenance for ongoing runs. Perform the following maintenance for every day in a calendar week after the first day that the instrument continues to run:

7.6.1. Check to see if the filtration membrane on the autosampler needs to be changed. This is indicated if you can see a heavy deposit of particulate on the underside of the membrane, in the grooves, or if you see reduced recovery of sulfate near the low end of the calibration curve (the CHCK5 is good for indicating this). If the membrane must be replaced, follow the steps in 7.5.8.2, except that you may wipe the grooves of the cartridge with DI water instead of with methanol. After the new membrane is installed, rinse with DI water for 300 seconds, as in 7.5.8.7.

7.6.2. Refill all three rinse bottles on the autosampler. If possible, dump the DI water rinse bottles, and rinse at least three times with DI water before refilling and replacing.

7.6.3. Check the suppressor rinse and regenerant bottles and refill if necessary. If possible, while the peristaltic pump is stopped, dump the rinse bottle, and rinse at least three times with DI water before refilling and replacing.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

7.6.4. Ensure you have enough eluent to continue your run. If not, replace the bag (or refill the bottle).

7.6.5. Check the system pressure as in 7.5.6.

7.7. Monthly maintenance. Perform the following maintenance once per calendar month, when starting the first run of the month:

7.7.1. Perform these steps when rinsing and/or refilling the suppressor rinse and regenerant bottles (instead of the procedure listed in 7.5.2.) and when rinsing and/or refilling the autosampler rinse bottles (instead of the procedure listed in 7.5.8.3. - 7.5.8.4.).

7.7.2. Dump the contents of the bottles.

7.7.3. Put a small amount of acetone (5-10 mL) in each bottle. Swirl the bottle to ensure that the walls and bottom of the bottle have been completely covered in acetone.

7.7.4. Let the bottles sit, covered, with the acetone in them for 30 minutes. This allows the acetone fumes time to kill any microbes.

7.7.5. Rinse the bottles at least three times with DI water.

7.7.6. Refill and replace the bottles as usual, and continue with regular weekly maintenance.

7.8. Quarterly maintenance. Perform the following maintenance procedures every three months (ideally, before the first runs in January, April, July, and October):

7.8.1. Replace each of the three inline filters. One is immediately after the high-pressure pump. The others are on the rinse and regenerant lines, immediately in front of the suppressor. The procedure is very similar to changing the RP guard disc, except that there is only a filter, no disc. See section 7.5.3.

7.8.2. Replace the peristaltic pump tubing bringing regenerant and rinse water to the suppressor. Use orange-yellow pump tubing for regenerant, and orange-white pump tubing for rinse. Cut the tubing in half between the anchors before placing it on the instrument; there should only be one anchor in use (on the upstream side). To avoid liquid siphoning out of the lines, remove the caps and lines from the acid and water bottles atop the instrument before changing the pump tubing.

7.8.3. Inspect the rollers on each peristaltic pump. Ensure that they are rolling freely. Disassemble and clean if necessary (see 7.10.2.).

7.9. Semiannual maintenance. Before the first runs of January and July, replace all tubing and fittings in the autosampler's flow path:

7.9.1. The tubing from the probe to the peristaltic pump, from the pump to the filtration cell inlet, from the underside of the filtration cell to waste, and from the injection valve to waste is PTFE tubing with an internal diameter of 0.97 mm, cut to length.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

7.9.2. The tubing from the filtration cell outlet to the peristaltic pump, and from the peristaltic pump to the instrument inlet is PTFE tubing with an internal diameter of 0.5 mm, cut to length.

7.9.3. The tubing from the instrument inlet to the injection valve is PEEK tubing with an internal diameter of 0.5 mm, precut at the factory to a 1 m length.

7.9.4. All fittings that screw directly into the filtration cartridge should be PVDF compression fittings. All other fittings should be PEEK compression fittings.

7.10. Annual maintenance Perform the following maintenance procedures once per year (ideally, at or just after the annual PM visit from Metrohm):

7.10.1. Schedule a yearly preventative maintenance visit with the Metrohm USA representative. For further information contact Metrohm USA at 1-888-92-TOTAL (1-888-928-6825).

7.10.1.1. Ensure that, during the PM visit, the Metrohm technician opens the injection valve and checks inside.

7.10.1.2. Be extra careful that, following the PM visit, the check valves of the high-pressure pump are seated correctly, and that the pump is properly primed and not slipping. Pump problems are not uncommon following the rebuilding of the pump at the annual PM.

7.10.2. The peristaltic pumps on the autosampler and instrument must be disassembled and cleaned. Instructions are in the Metrohm publication "Routine IC Maintenance Guide" (see section 13.6.), or you can ask the Metrohm technician to do this.

7.10.3. Replace all tubing in the instrument flow path or in the flow path of the regenerant or rinse. It is best to ask the Metrohm technician to do this.

7.11. Routine replacement of parts:

7.11.1. The housing that holds the RP guard disc has a projected lifespan of 6-8 months, so be sure to have a spare on hand at least when the current housing reaches 6 months old. When it fails, it is usually because the threading at the end of the guard screw has become deformed and no longer seals. Overtightening will shorten the housing's lifespan. Replace the housing when it becomes difficult to screw back together by hand. A new housing will come with an RP guard disc and supporting filter pre-installed.

7.11.2. The housings that hold the three inline filters are replaced in much the same way, and for the same reason, as the housing for the RP guard disc (See 7.11.1.). Their projected life expectancy is 1 year, because they are not normally opened as often.

7.11.3. The analytical column has a projected life expectancy of 1 year. Replace when peak resolution or baseline is too poor to continue use.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

7.11.4. The suppressor is warranted for ten years, and should not require replacement unless damaged by unusual circumstances.

7.11.5. The injection valve has a half-life of 5-7 years. It will require replacement if buildup on the groves within cannot be cleaned, or if it is scratched and can no longer seal.

7.12. The system is extremely susceptible to infestation by bacteria. To minimize the chance of this, do not swap parts or fluids (e.g. eluent, regenerant) between the two instruments.

7.13. If any significant changes are made to the system, such as a new column, change in eluent concentration, suppressor replacement, or change of flow rate, check the analytes' retention time and any interfering anion retention times by running the interference check standard. All peaks should be clearly resolved and well within the established retention time windows. When peaks elute too closely to the beginning or end of the window, large concentrations will cause the following sample baseline to fall.

7.14. Record in the maintenance log any maintenance carried out. Write down the serial numbers of all parts removed from or installed on the system. Also, place all service visit receipts in the maintenance log.

8. TROUBLESHOOTING

8.1. Incorrect system pressure:

8.1.1. The watch window allows you to continuously monitor system pressure. If you need to know historical pressure information, pressure is also saved with each chromatogram (open the chromatogram, then open Method>Passport and choose the "Eluent" tab). To check long-term trends in data exported to Autodatabase, there is a "Pressure Report." The system should normally run at about 5-7 MPa, depending on the age of the analytical column. If pressure goes above 10 MPa, the system will automatically shut down.

8.1.2. Pressure is directly proportional to flow rate. Make sure the pump's flow rate is set to 0.7 mL/minute. You can check the flow rate manually with a stopwatch and a graduated cylinder calibrated to contain. Collect eluent at the back end of the system, where it flows in to waste, or disconnect the pump from the injector valve and measure flow rate there.

8.1.3. The most likely cause of high pressure is a clog somewhere within the system. To find the clog, disconnect the eluent line that flows out of the pump from the inline filter. Turn the pump on and watch the pressure. Add the components of the IC, one at a time, in order.

8.1.4. The most likely places high pressure will be caused are:

8.1.4.1. The inline filter. This is easily corrected by changing the filter (See section 7.8.1.).

8.1.4.2. The RP guard disc (See section 7.5.3.).

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

8.1.5. The most likely causes of low system pressure are a leak somewhere in the system (See 8.4.) or air bubbles in the high-pressure pump. If the latter, the pump must be primed (see section 7.4.).

8.1.6. System pressure can also become inconsistent, fluctuating up and down. These fluctuations are often over long time intervals of several hours. This will often be first noticed by changes in retention time, especially affecting sulfate. The most likely causes of inconsistent system pressure are an air bubble in the pump head or a problem with the pump itself.

8.1.6.1. To remove an air bubble, first attempt re-priming the pump (see section 7.4.). If that fails, rinse the pump with methanol instead of eluent to remove the air bubble. Disconnect the pump from the rest of the system before attempting this, and ensure the methanol is fully rinsed out with eluent before re-connecting.

8.1.6.2. If the above procedure fails, attempt to remove and re-seat the pump's two check valves. The procedure for this is described in the Metrohm Publication "Routine IC Maintenance Guide" (see 13.6.).

8.1.6.3. If pressure is still fluctuating after the check valves are re-seated, the check valves will need replacement, or the entire pump will need to be rebuilt. Contact Metrohm USA.

8.2. Suppressor problems:

8.2.1. Suppressor problems can usually be detected if the baseline does not behave properly when the suppressor is stepped (see section 6.1.5.). The suppressor may also be at fault if the baseline sharply rises, goes off scale, and does not come back down.

8.2.2. The most common suppressor problem is leaking or restricted flow of regenerant and/or rinse. To check the flow rate of the regenerant and rinse, see 7.5.4.

8.2.2.1. The most common cause of restricted flow is the peristaltic pump tubing. Examine the tubing, as in 7.5.2. The problem may be corrected simply by turning off the peristaltic pump, then removing and re-seating the tubing. If that fails, changing the tubing may help (See 7.8.2.).

8.2.2.2. The couplings that connect the peristaltic pump tubing to other tubing may become deformed. If this is the case, they may restrict flow. Examine the couplings to see if one is squeezed shut. A deformed coupling can be replaced, or, if no replacement is available, opened with a narrow tool such as a pin.

8.2.2.3. The inline filters that regenerant and rinse pass through before entering the suppressor are another possible source of restriction. A filter can be easily changed (see section 7.8.1.).

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

8.2.2.4. If the rinse/regenerant bottle is disconnected from the peristaltic pump, the line should begin dripping as gravity siphons the liquid through the tube. If this does not happen, then the tubing is filled with air, and the peristaltic pump cannot generate enough pressure to prime it. Begin a siphon effect with a small transfer pipet, and then reconnect the tubing to the peristaltic pump.

8.2.2.5. Check all tubing in the restricted flow path. Tubing may become damaged and crimped, restricting flow. Any such tubing should be replaced.

8.2.3. Suppressor problems may also be observed if the suppressor has become unseated from its rotor. In this case, the baseline will not react at all when the suppressor is stepped, because the suppressor never turns. Eventually, this will cause the baseline to climb off scale and never come back down.

8.2.3.1. To determine if the suppressor is unseated, have a second person manually step the suppressor, while you keep your ear near it. If you hear a "click" sound instead of the normal "whirr" sound, the suppressor has become unseated.

8.2.3.2. To fix an unseated suppressor, you must remove it from its housing. Turn off all pumps when doing this. Unscrew the faceplate on the suppressor housing. Remove the suppressor. This may be quite difficult, as there is nothing to grip; it may be helpful to tilt the whole instrument forward. Push the suppressor back into place, and replace the faceplate.

8.2.3.3. If the suppressor still does not turn when stepped, the rotor may be stuck. You will need to manually free it. Remove the suppressor from its housing, as above. Take a Sharpie marker with the cap on, and insert the cap into the suppressor housing. You should be able to catch the notch that normally grips the suppressor with the pocket clip of the Sharpie. While a second person steps the suppressor, manually try and rotate the suppressor counter-clockwise by turning the marker. Repeat this procedure until the rotor is no longer stuck.

8.2.4. A baseline that gradually rises and goes off scale over a few injections, and never comes back down may be caused by a failure in the 853 CO_2 Suppressor. Check the lights on the unit to ensure that the "Power" and "Ready" lights are on. If the "Power" light is on, but the "Status" light stays on for an extended period of time, and is never replaced by "Ready," the unit is not removing CO_2. The most probable cause is that the carbon dioxide absorber cartridge requires replacement (See 7.5.5.2.).

8.3. If peaks are too small or there are no peaks, check to ensure that samples are being injected properly. Check the flow of filtrate out of the filtration cell. Problems with the filtration cell may be caused by the filter, which can easily be changed; or by the peristaltic pump tubing, which can be easily replaced (see

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

7.5.8 to change either.). Ensure that the pump tubing that carries filtrate to the loop is not hooked to the peristaltic pump backwards – this is a surprisingly easy mistake to make. If only some peaks are too small (e.g., low-level sulfate), check to see if the filtration membrane requires changing.

8.4. Leaks:

8.4.1. The easiest way to detect a leak in the system is via the leak detector, which will send an error to the watch window if it detects liquid in the bottom of the instrument's cabinet.

8.4.2. A leak in the system may be easily repaired by replacing the leaking part. If the leak occurs at a connection that was recently opened, it may simply need to be tightened.

8.4.3. A leak in the housing for an inline filter or the RP guard disc most likely indicates that the housing needs to be replaced (See 7.11.1. - 7.11.2.)

8.4.4. A leak that persists or recurs may indicate that there is a blockage farther downstream. See section 8.1. Note that, in this case, system pressure may be reading normally, since the leak may relieve the high pressure caused by the blockage.

8.4.5. If the peristaltic pump tubing for the suppressor develops a leak, disassemble and clean the peristaltic pump head (see 7.10.2.) as soon as possible. Liquid left inside the pump head can cause worsening corrosion.

8.5. Problems following injection of a high sample:

8.5.1. If a sample that is extremely high in ions is injected without dilution, it can cause problems for subsequent injections.

8.5.2. The most common problem is carryover. If peaks continue to be elevated in subsequent injections, replace the autosampler's pump tubing and filtration membrane and rinse (see 7.5.8.). It may be necessary to rinse for longer than the normal 300 seconds.

8.5.3. If you begin seeing malformed peaks or a malformed baseline, the sample may have overloaded the RP guard disc, which will have to be changed (see 7.5.3.). You may also need to change the inline filter immediately downstream of the high-pressure pump (see 7.8.1.).

8.5.4. It is unlikely that a single injection would damage the column; the RP guard disc should prevent that. However, multiple high injections might. If problems from a high injection persist after taking the steps above, you may need to clean the column (see 8.8.) or even replace it.

8.6. Malformed peaks or baseline:

8.6.1. Malformed peaks, misshapen (e.g., convex) baselines, and recurring baseline shifts are likely caused by problems with the suppressor or column.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

8.6.2. Split peaks often indicate a void on the column. If this is the cause, the column must be replaced.

8.6.3. It is best to begin troubleshooting these problems by replacing the RP guard disc (see 7.5.3.). Inline filters (see 7.8.1.) may also require changing. If these fail, it may be worthwhile to attempt changing the eluent.

8.6.4. The likely solution to these problems will be cleaning the column (see 8.8.), replacing the column, cleaning the suppressor (see 8.7.3.4.), or replacing the suppressor.

8.7. Chromatography Problems:

8.7.1. A wide variety of problems can produce chromatograms that look good (good resolution, good integration, good peak shape, etc.), but calibrations that are not usable. These problems usually affect sulfate earlier and more severely than the other analytes.

8.7.2. When faced with such a problem, first try the simplest and quickest solutions. Replace the eluent, re-make standards and reagents, replace the filtration membrane and pump tubing on the autosampler (see 7.5.8.), replace the RP guard disc (see 7.5.3.) and the inline filter just downstream of the high-pressure pump (see 7.8.1.). Check all flow rates (see 7.5.4., 7.5.8.8., and 8.1.2.). Check the system pressure and review recent pressure changes (see 8.1.1.). Examine peak integration to make sure it is correct (see 8.10.).

8.7.3. Contamination by metals or organics:

8.7.3.1. If you have recently run samples that were high in metals or organics, the instrument may be contaminated with them.

8.7.3.2. This sort of contamination can cause high system pressure. It can also cause chromatography problems.

8.7.3.3. The RP guard disc is most likely to be affected by this problem, since its function is to remove these sorts of contaminants. Replacing it (see section 7.5.3.) may solve the problem.

8.7.3.4. Metal contamination on the suppressor can be cleaned with an oxalic acid solution passed through the suppressor in the reverse of the usual flow direction. Complete instructions are in the Metrohm publication “Cleaning Procedures for Iron Contamination” (see 13.7.). That document also contains cleaning procedures using oxalic acid to remove metals from the flow path (without the column) and from the injection valve. Note that the duration of these cleaning procedures or any other cleaning procedures that do not involve the column, may be increased; the longer the cleanup is performed, the greater its effectiveness.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

8.7.3.5. If the contaminants have gotten onto the column, you may attempt to clean it (See 8.8.).

8.7.4. Bacterial growth:

8.7.4.1. Bacteria can grow in the carbonate/bicarbonate eluent and cause serious problems.

8.7.4.2. Bacteria can cause chromatography problems. They also can cause baseline problems – a "rolling" baseline that gradually rises and falls may be indicative of a bacteria problem. Bacteria may also be detected by looking for discoloration in tubing that should be clear.

8.7.4.3. Bacteria can be cleaned out of the system following these instructions:

8.7.4.3.1. Remove the column and replace it with a female-female coupling. Remove and discard the guard column and replace its housing (empty) onto the instrument.

8.7.4.3.2. Replace the normal eluent with a 20 % methanol solution, and the normal regenerant with a 0.5 M solution of sulfuric acid in 50 % acetonitrile.

8.7.4.3.3. Ensure the valve is in the inject position. Run the cleaning solutions through the instrument for at least an hour, stepping the suppressor twice during cleaning so that each suppressor chamber is cleaned for one-third of the time. Note that the duration of this cleaning procedure, or any other cleaning procedure that does not involve the column may be increased; the longer the cleanup is performed, the greater its effectiveness.

8.7.4.3.4. During this time, remove the autosampler's filtration membrane and replace the cell, empty, onto the autosampler. Replace the normal contents of the autosampler's rinse bottles with a 20 % methanol solution and run this through the flow path for an hour (or more, as above). It is best to replace all tubing and fittings on the autosampler if bacterial contamination has become established (see 7.9.). Cleaning the filtration cartridge and probe in 20 % methanol in an ultrasonic bath has also proven effective.

8.7.4.3.5. Once cleanup is done, replace the cleaning fluids with normal fluids (eluent, regenerant, rinse) and run to re-equilibrate. Be sure that all cleaning solutions have been rinsed from the instrument before replacing the column and putting on a new RP guard disc. It is best to change all inline filters at this time as well.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

8.7.4.3.6. The column must be cleaned separately from the rest of the flow path, see 8.8.

8.8. Cleaning the column:

8.8.1. The analytical column should be cleaned only when needed because contamination of the column is suspected.

8.8.2. For detailed information on column cleaning, please refer to Metrohm USAs' "Column Cleaning Procedure" (see 13.4.). This document should be read and understood before attempting column cleaning.

8.8.3. When cleaning the column, rearrange the system so that the flow from the pump will go directly into the *analytical* column, bypassing the RP guard disc and the injector valve. The flow from the analytical column should go directly to waste. It is best if the outlet of the column goes *directly* into a waste container, rather than into a length of tubing routed to a waste container.

8.8.4. Do not reverse the direction of flow through the column when cleaning! The eluent should flow through the column in the direction indicated by the arrow on the outside of the column.

8.8.5. Do not let the effluent from the columns (cleaning solution) flow into the suppressor. When cleaning, disconnect the suppressor and conductivity cell from the system completely, bypassing them. Let the cleaning solution flow into waste.

8.8.6. When cleaning, the pump rate will need to be changed. A cleaning solution will be used in place of normal eluent. Precise details will vary depending on the suspected contamination. See "Column Cleaning Procedure."

8.8.7. Injecting two immiscible liquids onto the column in immediate succession can destroy the column. Be sure that if you are about to inject a solution onto the column that it is miscible with the solution already on the column. If not, flush the current column contents with an intermediate rinse.

8.8.8. Unlike other cleanups, the duration of column cleanups should not be increased.

8.8.9. Iron (or other metal contamination) - Metal contamination on the suppressor can be cleaned with an oxalic acid solution. Complete instructions are in the Metrohm publication "Cleaning Procedures for Iron Contamination" (see 13.7.).

8.8.10. Bacterial infestation:

8.8.10.1. Connect the column directly to the pump, and route the column outlet straight to waste, as described above.

8.8.10.2. Change high-pressure flow rate to 0.3 mL/minute.

8.8.10.3. Pump DI water through the column for 30 minutes.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

8.8.10.4. Pump either 20 % methanol or 20 % acetonitrile through the column for 2-3 hours.

8.8.10.5. Pump DI water through the column for 30 minutes.

8.8.10.6. Pump eluent through the column for 15 minutes.

8.8.10.7. Return the instrument to its regular configuration, but leave the flow rate at 0.3 mL/minute.

8.8.10.8. Turn on the pump and the peristaltic pump. Every 5 minutes, increase the pump flow rate by 1 mL/minute, until it is back at its normal 0.7 mL/minute. System pressure will initially be high, but, about an hour after normal flow rate is reached, it should be normal. Remember during this procedure to step the suppressor periodically (see 6.1.5.).

8.8.11. After any column cleanup, it is best to let the column equilibrate for 16 hours before attempting to use it. During this time, inject blanks to keep the suppressor stepping regularly.

8.9. Software Problems:

8.9.1. Most software problems can be solved by rebooting the computer. This will, of course, interrupt data collection or execution of a sample queue, so be sure, if possible, to pause the queue and allow the current chromatogram to be completed before attempting this. Rebooting the computer will *not*, however, cause the instrument to shut down.

8.9.2. If rebooting the computer alone is not sufficient, try powering down the entire system (instrument and computer), and then powering up again (see 6.1.). This will, of course, cause the instrument to shut down. The most common error that necessitates this step is a COM port error that prevents the software from establishing an initial connection to the instrument.

8.9.3. If the sample queue becomes locked after editing, exit the queue editor, and abort the queue by selecting Control>Abort from the menu in the queue window. Afterwards, you can reopen the queue and start it as normal.

8.10. Integration problems:

8.10.1. As the column ages, retention times gradually lessen. This can cause peaks to be mis-integrated. Retention time windows and integration and data parameters may have to have their timing slightly adjusted because of this.

8.10.2. Retention times can be changed in the method file under Calibration > Components.

8.10.3. Integration parameters can be changed in the method file under Integration > Events. Each event has a time associated with it. These times can be changed to move the event slightly.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

8.10.4. Remember, when changing retention times or integration parameters, the same values must be used for every chromatogram on a run! Otherwise, you are manually integrating the chromatograms that you are changing.

8.10.5. The maximum range of the conductivity detector changes between the chloride and nitrate peaks. This creates a visible dip on the chromatogram. If the nitrate or bromide retention time lessens, this dip can interfere with integration of those peaks. To move this dip, you must edit each of the system files in use. Open the system file, double click on the instrument, and open the "Program" tab. The event to be moved is "FullScale: 50 µS/cm." Be sure to move it by the exact same amount of time in every system file! Also, this dip is excluded from integration in the Integration Events; be sure to change the times there to reflect the time change of the dip.

8.11. If the peristaltic pump is not injecting properly, and replacing the peristaltic pump tubing does not correct the problem, it may be necessary to clean the pump (see 7.10.2.).

8.12. If you cannot solve a problem yourself, call Metrohm USA (See section 7.10.1.).

8.13. Record in the maintenance log any troubleshooting carried out. Explaining how a problem is solved may help solve future problems more quickly.

9. POST-RUN PROCEDURE

9.1. IC Net uses a technique called "batch reprocessing" to treat a large group of chromatograms the same way, and attach the same method file (integration parameters, calibration curve, etc.) to all of them. When a run is complete, put all of the chromatograms in the run into the same batch. To do this, select File>Open>Chromatogram. Select all of the chromatogram files in the directory, and then click the <To Batch> button. IC Net will prompt you for the name of the batch; name it after the date the run started (in the format yymmddic). You will need to generate separate batches for chloride/sulfate, bromide, and nitrate. Append "-cs," "-b," or "-n" to the filename. From now on, you can re-open this batch quickly by selecting File>Open>Batch Reprocessing.

Note: If you have a long sequence report for sulfate/chloride, and only a few lines of it pertain to nitrate or bromide, you don't have to include *all* of the data in the nitrate or bromide batches. Only select the calibration curve, the run QC, and the lines that pertain directly to the nitrate or bromide samples (including the flanking CCVs and CCBs).

9.2. Whenever you assign chromatograms to a batch or open an existing batch, the batch reprocessing window will open. At the top of this window, there is a drop down-menu to select the file from which the method will be applied. This will normally be the L1, the first chromatogram on the run. If you are sure that this file contains the integration and calibration parameters you want to use, select the check boxes for "Reintegrate" and "Recalibrate." Also make sure that the appropriate check boxes are selected to reprocess both sample and calibration runs, forget existing calibration points, and apply the new curve to all files. Then,

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

click the <Reprocess> button. This will reintegrate and recalibrate all of the files using the parameters from the file you selected.

9.3. Most reports from the data are generated using Microsoft Excel.

9.4. Open the batch that contains the data for the run. Check the box that says "Recalculate only." Check the box that says "Make Report." Click the <Edit report options> button. In the "Template" field, select the template that matches the components you are exporting. There are three: CS_seq.rtt for chloride and sulfate, B_seq.rtt for bromide, and N_seq.rtt for nitrate. In the "Report Destination" section, check the box that says "File." In the "Items to report" and "More items to report" sections, ensure that the only check box selected is "Peak Table". This will export all of the run data to the Excel file when you reprocess. The appropriate Excel file will open automatically.

9.5. The report must contain a printout of all calibration curves and of the method file. This information is attached to every file, so select any chromatogram from the run. Instead of opening the file, send it to a batch by itself. You won't need to keep this batch, so you can give it a name of "" (i.e., a blank field); be careful not to overwrite the batch you generated for the run. Check the box to "Recalculate only," and check the box to "Make Report." Click the button to <Edit report options>. In the report window that opens, set the value of the "Template" field to "English.rtt." Make sure the following check boxes are checked (these are things to be included in the report) - Column, Eluent, Acquisition, Integration, Calibration defaults, Component table, and Calibration results. Make sure the check box is marked that will send the report directly to the printer. When you reprocess, the report that prints out will be a hard copy of the method file, plus printouts of each calibration curve.

9.6. The report must contain a printout of the sequence report. This is simply a printout of the Excel file generated in 9.4. There is a "Clear" button in this file. Click it to save the data into a new file, specific to the run, and empty this file so that the next run can be exported into it. Save the new file in the same directory as the chromatograms for the run. Use the same naming convention you used to name the batches (See 9.1.). Print from the newly saved file. Be sure to delete the "Clear" button first, or it will appear on the printed report.

9.7. You can also generate an export file for QC Manager from the same file. Simply save the Excel file in CSV format to \\FLDEP1\DEAR\LABS\lab3\Chem_Data\Inorganic\Nutrients\Metrohm_IC\ Give the file a name based on the date the run started, using the format YYMMDDIC#, where # indicates the instrument used.

9.8. The report must contain a printout of some of the chromatogram files. The chromatograms that must be printed are the entire calibration curve and the run QC (i.e., the interference standard, the CHCK1, ALTQC, the MDL standard, the first PQL standard on the run, the first CCV on the run other than the CHCK1, and the first CCB on the run). Open each of these chromatograms, and make sure they are scaled appropriately for printing. Then send all of these chromatograms to a batch. You won't need to keep this batch, so you can give it a name of ""

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

(i.e., a blank field); be careful not to overwrite the batch you generated for the run. Check the box to "Recalculate only," and check the box to "Make Report." Click the button to <Edit report options>. In the report window that opens, set the value of the "Template" field to "English.rtt." Make sure the following check boxes are checked (these are things to be included in the report) - General, Sample, and Chromatogram plot. Make sure the check box is marked that will send the report directly to the printer. When you reprocess, each of these chromatograms will be printed out.

9.9. The report should also contain a standard sheet showing the serial number, name, and expiration date for each standard used on the run. A reagent sheet must also be present, showing the serial numbers of all reagents used or of the stocks used to make them, as well as preparation and expiration dates.

9.10. The report must also include the following - the MDL and PQL values for each component reported, the values and spiking method for each spike code used, the dilution method for each dilution factor used, and the name and serial number of the instrument on which the run was performed. For soils the extraction is documented using the Prep Worksheet Manager module of LIMS. The preparation worksheet ID must be included in the report (see DEP SOP NU-044).

9.11. If the integration parameters are set appropriately in the method file, the amount of manual reprocessing will be minimal. Try to manually reprocess as few chromatograms as possible. If a chromatogram must be manually reprocessed, note this on the sequence report, along with an explanation of the reason. Print out a copy of the chromatogram with and without manual reprocessing applied and include them in the report. For the chemistry section's policy on manual integration, see DEP SOP CM-018.

9.12. Convert the text file into the QC Manager, and complete the calculations and data uploading from QC Manager.

9.13. Move the directory containing the chromatogram files, Excel file, and batch file from the hard drive of the IC Net computer to the network. Metrohm data is stored in the appropriate folder for the IC instrument used, \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\Metrohm_IC\IC1\ Data\ and \Nutrients\ Metrohm_IC\IC2\Data\. Place the directory into the appropriate subdirectory for month and year.

10. DATA ARCHIVAL

10.1. The raw data is archived in paper format. A report folder is created for each analytical run. Occasionally more than one run may be in one folder. The folder is labeled with the test (IC-SO4, Cl, etc.), filename/s (YYMMDDIC#-LL, where # indicates the instrument used and -LL indicates the components reported in the run. CS stands for sulfate and chloride, B for Bromide and N for nitrate), and initials of the analyst.

10.2. Each report folder should contain the following items - the calibration reports with method parameters, results report(s), MDL/PQL values and spike codes, etc.,

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

bench sheet(s), reagents and standard sheets, chromatograms for initial QC, and notes or comments, and a copy of the data and QC assessments uploaded from QC Manager to LIMS at the time of test authorization.

10.3. The report folders are on file with the nutrients and general chemistry supervisory personnel. Periodically, the files are moved to the State Records Center for long time storage according to DEP SOP LB-006.

10.4. IC instrument data excel transfer files for upload to QC manager are stored in electronic format located on the Nutrients drive: \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\Metrohm_IC\.

11. SAFETY/HAZARDOUS WASTE MANAGEMENT/POLLUTION PREVENTION

11.1. Review the Laboratory Health and Safety Plan (accessible on the intranet at https://www.fldepnet.org/content/dear/bureau-laboratories-safety-documents).

11.2. Safety glasses, gloves and lab coats should be worn at all times while handling samples and reagents.

11.3. Read the MSDS information for safe reagent and sample handling.

11.4. The IC analysis does not normally generate hazardous waste, so the eluent and sample waste can go down the drain. The Metrohm may be set up to flush waste directly into a sink, or the waste can be directed into a plastic carboy that is emptied as needed.

12. QUALITY CONTROL/DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES (SEE DEP SOPS NU-038 AND NU-043)

12.1. For method performance and acceptance criteria for QC measures, corrective action for out-of-control data, and contingencies for handling out-of-control or unacceptable data, refer to the following DEP SOPs NU-038 and NU-043.

12.2. A new calibration is performed at the beginning of every analytical run. The working calibration range is verified every time a new calibration is performed. The correlation coefficient for every component reported must be equal to or larger than 0.995. The acceptance limits for the recoveries for each calibrant above the PQL are 90 - 110 %. For general information, see the FDEP Bureau of Laboratories Quality Manual, Appendix B, Section 7.0, Technical Requirements and for the linear calibration range see Section 7.1.1, ‘Protocol for Determining the Test Method Range of Applicability’.

12.3. Certain QC samples must be run at the beginning of every run sequence. These are:

12.3.1. A second source (ALTQC, see 4.9.). The acceptance limits for the recovery of the ALTQC are 90 - 110 %.

12.3.2. A PQL-level check standard (see 4.7.). Acceptance limits for the recovery of the PQL are 70 - 130 %.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

12.3.3. A MDL-level check standard (see 4.7.). There are no defined acceptance limits for MDL-level standards, but all analytes must be detected and each must be readily distinguishable from the PQL-level standard for that analyte.

12.3.4. An Interference Check Standard, which has acceptance limits of 85 - 115 % recovery. This should be run with a CHCK1, which has the same levels of each analyte. That way, if there is a failure in the Interference Check Standard, the analyst can tell if it is related to interference or a calibration problem. The acceptance limits on the CHCK1 are 90 - 110 % recovery (since it is a CCV, see 12.4.1.).

12.3.5. A blank to check for carryover. This is simply DI water, and is run immediately after the highest calibration standard. Carryover from high samples is not usually observed on this instrument, but can occur if the filtration membrane is not being adequately rinsed between injections. The carryover blank has the same acceptance limits as other blanks (see 12.4.2).

12.3.6. A CCV with the same values as the upper limit of calibration, the CHCKHI2. This has the same acceptance limits as other CCVs, 90 - 110 % recovery.

12.4. Each run should include a CCV and a CCB (DI water) every 10 samples (i.e. every 12^{th} cup).

12.4.1. For the CCV, alternate the CHCK2 and CHCK5 standards (see 4.7.). Acceptance limits for the recovery of the check standards are 90 -110 %.

12.4.2. Results for all blanks (CCB/BLK) should be less than the MDL and greater than –MDL.

12.4.3. Remember, a reportable result must be flanked by passing CCVs and CCBs.

12.5. Certain QC must be run for every batch of up to 20 samples:

12.5.1. A method blank (MBLK). This consists of DI water that is prefiltered with a syringe filter. See 12.4.2. for the acceptance limits.

12.5.2. Precision must also be demonstrated so run either a duplicate sample or duplicate matrix spike (see 12.5.3.) with each batch of 20 samples to demonstrate that the relative percent difference (RPD) is < 20 %.

12.5.3. For each batch of 20 samples, two matrix spikes of different samples and an LFB must also be analyzed to ensure that analyte recovery is within acceptable ranges (see section 5.6). Follow the standard spiking protocol for duplicates and spikes. Acceptance limits for matrix spike recoveries and LFB recoveries are 90 - 110 % for aqueous matrices, and 80 - 120 % for solid matrices.

Spike a 10 mL aliquot of sample (or DI water for LFBs) with all analytes for each level. Generally, spike level N3 is used unless information about

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

a sample suggests another level would be more appropriate. The following quantities are used:

Spike N1:

Analyte	Spike Level (mg/L)	Stock Conc. (mg/L)	Amount of Stock (µL)
Sulfate/Chloride	10	10,000	10
Nitrate	0.50	100	5

Spike N2:

Analyte	Spike Level (mg/L)	Stock Conc. (mg/L)	Amount of Stock (µL)
Sulfate/Chloride	20	10,000	20
Nitrate	1.0	1000	10
Bromide	0.1	100	10

Spike N3:

Analyte	Spike Level (mg/L)	Stock Conc. (mg/L)	Amount of Stock (µL)
Sulfate/Chloride	30	10,000	30
Nitrate	5.0	1000	50
Bromide	0.5	100	50

Spike N4:

Analyte	Spike Level (mg/L)	Stock Conc. (mg/L)	Amount of Stock (µL)
Sulfate/Chloride	40	10,000	40
Nitrate	2.0	1000	20
Bromide	0.2	100	20

Spike N5:

Analyte	Spike Level (mg/L)	Stock Conc. (mg/L)	Amount of Stock (µL)
Chloride	50	10,000	50

12.6. The IC can run over more than one day if the calibration range is checked and confirmed to be acceptable. This can be done by running a PQL standard at least every 24 hours.

12.7. If the instrument has not injected a sample for an hour or more, or the pump has shut down and been re-started, the calibration must be checked before running new samples. This is done by running a CCV, a PQL standard, and a CCB.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

13. REFERENCES/DEFINITIONS/VALIDATION DATA

For definitions see section 3 of the FDEP Quality Manual. All abbreviations used throughout the document are defined at least once in the document usually at the first time of use. Method validation data is on file with the supervisor. The limit of detection (LOD) is verified on every run based on the PQCK5.

13.1. Autosampler manuals:

13.1.1. 788 IC Filtration Sample Processor: Instructions for Use, Metrohm AG, 2001. Document 8.788.1003.

13.1.2. 838 Advanced Sample Processor: Instructions for Use, Metrohm AG, 2005. Document 8.838.1013.

13.1.3. 838 Advanced Sample Processor: Installation Instructions, Metrohm AG, 2005. Document 8.838.1313.

13.2. IC manuals:

13.2.1. 761 Compact IC: Instructions for Use, Metrohm AG, 2000. Document 8.761.1023.

13.2.2. 861 Advanced Compact IC: Instructions for Use, Metrohm AG, 2005. Document 8.861.1033.

13.3. 853 CO_2 Suppressor: Instructions for Use, Metrohm AG, 2005. Document 8.853.1003.

13.4. "Column Cleaning Procedure," Metrohm USA Technical Service Department, 2005.

13.5. Metrodata IC Net 2.3 SR4 Software Manual, Metrohm AG, 2006. Document 8.102.0033.

13.6. "Routine IC Maintenance Guide v. 2," Metrohm USA Technical Service Department, 2010.

13.7. "Cleaning Procedures for Iron Contamination in a Suppressed Anion System," Metrohm USA Technical Service Department, 2010.

13.8. EPA Method 300.0 Rev. 2.1 (1993).

13.9. DEP SOP NU-033, Summary of Sample Analysis Procedures for the General Chemistry and Nutrients workgroups.

13.10. DEP SOP NU-038, Nutrients and General Chemistry: Quality Assurance and Quality Control.

13.11. DEP SOP NU-041, Reagent Preparation Procedure.

13.12. DEP SOP NU-042, Standard Preparation Procedure.

13.13. DEP SOP NU-043, Nutrients and General Chemistry Quality Assurance and Data Authorization Guidelines

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

13.14. DEP SOP NU-044, Aqueous Extraction of Orthophosphate, Nitrate, Chloride, and Sulfate from Soils and Sediments.

13.15. DEP SOP CM-018, Laboratory Policy Regarding Manual Chromatographic Peak Integration.

13.16. DEP SOP LB-006, Standard Operating Procedure for Records Maintenance and Storage.

13.17. Quality Manual, Bureau of Laboratories, FDEP.

13.18. Laboratory Health and Safety Plan.

Note: Hard copies of references 13.1 through 13.5 are kept in the laboratory in the manuals drawer or in a rack above the computer. Electronic copies of references 13.6 and 13.7 are on the network.

Appendix of Significant Changes

08/27/2010 Sulfate MDL for solids was added to Section 1.1.

08/29/2011 Added expiration, received and opened date requirements for the certified eluent bags and edited the Metrohm technical support phone number. Section 11.2. was modified to explicitly mention the verification of the working calibration range with every run.

09/04/2012 Maintenance items added to Section 7.0 and troubleshooting items added to Section 8.0.

05/15/2013 The SOP was extensively modified in many sections to add the Bromide test and cleaning/maintenance procedures to avoid bacterial and iron contamination.

05/01/2015 The title of Section 9 was changed to “Post-Run Procedure”. Data archival information was clarified in Section 10. Information about the Bromide Stock standard was added to Section 4.

05/24/2016 The upper limit of calibration for sulfate and the bromide stock standard were changed, with associated updates to the instructions in Section 4.6.5 and Table 1. Section 7.5.5. was updated for the single CO2 suppressor cartridge now in use. File paths were updated.

11/15/2018 Retired SOP NU-083-1.10 was reissued as SOP NU-102-1.0 due to a breakdown of the Dionex IC instrument.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.