KCL EXTRACTION OF NITRATE/NITRITE AND AMMMONIA FROM SOILS AND SEDIMENTS

1. SCOPE AND APPLICATION

1.1. Ammonia and nitrate-nitrite are extracted from sediment samples using a KCl extraction technique.

1.2. The resulting acidified aqueous extract is analyzed as a water sample using the appropriate analysis methodologies (for ammonia see DEP SOP NU-015, for nitrite/nitrate see DEP SOP NU-019).

2. SUMMARY OF THE METHOD

A subsample of the soil or sediment is mixed with KCl extraction solution using an automated shaker and allowed to settle. The extract is then decanted, acidified and analyzed by the appropriate analytical method.

3. APPARATUS AND EQUIPMENT

3.1. Platform shaker

3.2. Nalgene disposable wide mouth 250 mL bottles with cap

3.3. 50 mL polypropylene centrifuge tubes

3.4. 100 mL graduated cylinder (Class A) or a bottle-top dispenser.

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

Note: Archive the preparation of the reagents and standards in the Standard Preparation Tracker in the Laboratory Information Management System (LIMS). Unique ID numbers for each reagent and standard are generated in the module and documented in the extraction prep worksheet created in LIMS. A Certificate of Analysis for each purchased standard is maintained in the binder kept in C307. Certificates of Analysis for reagents are archived in the REAGENT_PREP folder on the Nutrients drive. All containers holding reagents or standards must be labeled with their unique ID and expiration date. See the appropriate analysis SOP for specific information about reagents and standards.

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

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4.1. Chemicals:

4.1.1. Potassium chloride, KCl

4.1.2. Deionized (DI) water

4.1.3. Ottawa Sand Standard (20-30 mesh), for blanks and laboratory fortified blanks (LFBs).

4.1.4. Conc. sulfuric acid, H_2SO_4.

4.2. Reagents and Standards:

4.2.1. KCl extraction solution - In a 2 L volumetric flask, dissolve 300 g of KCl (4.1.1.) in DI water. Dilute to the mark. A large carboy may be used when making l**a**rge quantities of extraction fluid. Holding time, 30 days.

4.2.2. For spiking stock standard preparation instructions refer to the supervisor or chemist of the appropriate analysis. See also DEP SOP NU-015 for ammonia and DEP SOP NU-019 for nitrate/nitrite. In general, sediment spike levels are based on the expected sediment analyte concentration and are often 5 - 10 times higher than spike levels for analysis of water samples. Sandy samples are usually spiked at two levels: 0.5 mg N/L for S-NH3 or 1.0 mg N/L for S-NO2NO3 (low-level spike, spike code S1), and 5 mg N/L for S-NH3 or 10 mg N/L for S-NO2NO3 (high-level spike, spike code S2). Other spike levels and codes may be applied as needed.

5. SAMPLE HANDLING AND PRESERVATION

Extracted samples are stored in the refrigerator at ≤ 6°C (not frozen). The acidified extracts must be analyzed within 28 days of sample collection.

6. SAMPLE PREPARATION (SEE DEP SOP NU-033)

6.1. Create a new extraction prep worksheet which can be found under the prep ID "EXT-KCL" in the Prep Worksheet Manager module of LIMS. Complete the upper part of the sheet, which contains some general information including: worksheet and prep IDs, analyst's name, SOP (NU-052), spiking solution unique ID number and units, start and completion date and time of the extraction, shaker equipment ID, balance ID, reagent unique ID numbers, prep comments, and review information. Update the sample grid table below the general information section. Add spike codes and amounts for spiked samples, serial numbers for the standard solutions used, sample wet weights,

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reagent amounts, and sample comments (if needed). Make sure test IDs and other auto-filled information such as standard names, matrix, % solid, and reprep info for samples are correct and updated. Check that sample dry weight calculations are correct. Prep batch IDs are assigned in the worksheet. Ask a supervisor to review the worksheet.

6.2. Sample homogenization (for soils and sediments) - If the sample cannot be thoroughly mixed within its container without spilling, empty the entire sample into a stainless steel tray. Remove any rocks, shells, twigs, leaves, etc. from the samples and mix thoroughly to achieve homogeneity. A mortar and pestle may be used to break up any clumps. Return the sample to the jar.

6.3. Weigh out 10.0 g of sample into a pre-labeled 250 mL container. The weight of sample used may be adjusted depending upon the concentration of analyte expected. Record all weights in the prep worksheet.

Sample weighing procedure:

- Check the maintenance book of the balance to confirm that the balance calibration was checked on the day you intend to use it. If it was not done, perform balance calibration checks (see DEP SOP CM-011 for detailed instructions). Record the balance ID in the prep worksheet.
- Place a pre-labeled 250 mL container onto an analytical balance and tare the balance so that it reads 0.0000 g. Using a clean stainless steel spatula, carefully transfer enough homogenized sample to the weighing boat to yield 10.0 g +/- 0.1 g of material. The QC sample (duplicates and/or spikes) weights should be within 0.05 g of each other. Record the weight under "sample wet weight" in the prep worksheet, and check the % solid information and calculated sample dry weight for each sample.

Note: If sample is to be reported in units of dry weight (mg/kg), the % solid determination should be performed prior to extraction so that the correct sample weight may be determined.

6.4. For every batch of 20 samples, one method blank (MBLK), one laboratory fortified blank (LFB), a sample in duplicate, two low-level spikes and one high-level spike are extracted. One practical quantitiation limit (PQL) standard (PQCK2) and one standard reference material (SRM) are extracted per extraction tray.

6.5. For the MBLK, PQCK2, and the LFB samples - Weigh out 10.0 g of Ottawa sand as sample matrix into a pre-labeled 250 mL container.

Note: If found to be contaminated, the Ottawa sand standard should be cleaned as follows. Add amount of sand needed for analysis to a 250 mL bottle. Add 100 mL of 50 % HCl solution and shake on a platform shaker for 30 minutes at 150 - 200 rpm. Decant off

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acid solution, and rinse sand 5 times with DI water. Add 100 mL DI water and shake for 30 minutes as described before. Decant off DI water and place clean sand in a glass jar. Dry overnight at 60 ºC.

6.6. Weigh out an appropriate amount of SRM sample into a pre-labeled 250 mL extraction container. The amount depends on the concentration of the SRM. Consult your supervisor and the Certificate of Analysis for SRM.

6.7. Add spiking solution to the PQCK2, LFB, and samples selected for the matrix spikes. (See DEP SOPs NU-015 and NU-019 for spiking solutions and concentrations).

6.8. With a graduated cylinder, carefully add 100 mL KCl extraction solution (4.2.1.).

6.9. Shake on the mechanical platform shaker for 30 minutes at 150 -200 rpm. Record the start day/time of the extraction in the prep worksheet. The start day/time is when the samples are placed on the shaker.

6.10. Let the sediment settle overnight in the refrigerator and decant 50 mL of the liquid into a pre-labeled 50 mL centrifuge tube. Record the finish day/time of the extraction in the prep worksheet. The finish day/time is when the last sample has been decanted.

6.11. Preserve each sample by adding 100 µL of H_2SO_4 (4.1.4.) immediately. Cap the tube and invert several times. The concentration of $H2SO4$ in the preserved aliquot should be 0.2 % (2 mL H_2SO_4 per liter total volume).

6.12. Make sure that the prep worksheet in LIMS has been reviewed, then complete the worksheet; this changes sample status from “W” to “V”. Attach the prep worksheet ID to the sample tray.

6.13. Store the extracts in a sample refrigerator in the receiving room (C201, refrigerator #10 shelf 10-6-3). Samples/extracts must not be stored in refrigerators containing standards. Samples for ammonia analysis should be well sealed to prevent loss of analyte through volatilization.

6.14. When analyzing the extracts, pre-filter the aliquot to be analyzed using a syringe filter with a 0.45 µm nominal pore size. Also, analyze a filtered blank and check standard with this type of syringe filter.

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

An extraction batch is defined as a set of 20 samples or less. Each extraction batch must be prepared with its own set of QC samples. See relevant analytical SOP (DEP SOP NU-015, DEP SOP NU-019) or supervisor for QC acceptance limits (1.2.).

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7.1. Extraction MBLKs, LFBs, PQCK2, and SRM - One MBLK and one LFB must be extracted per batch of twenty samples or less. One PQCK2 and one SRM are extracted per tray of samples. The MBLKs, LFBs, and the PQCK2 QC sample are prepared in the same way as a sample, using Ottawa sand as the matrix.

7.2. Sample duplicates (Precision) - One sample is chosen as the quality control sample for each batch and is run in duplicate. The precision may be determined from a sample duplicate or a spike duplicate. Generally, because the concentrations of the analytes are not known in advance, both sample and spike duplicates are prepared for each batch, using the same sample for the sample duplicates and to prepare the matrix spikes (7.3.).

7.3. Sample matrix spikes: The QC sample selected in section 7.2. is also spiked with NH_3 and NO_2/NO_3, twice at a low-level and once at a high-level spike concentration.

7.4. Waste samples should be batched separately from soils and sediments.

8. SAFETY/HAZARDOUS WASTE MANAGEMENT/POLLUTION PREVENTION

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

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

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

9. REFRENCES

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.

9.1. Quality Manual, Bureau of Laboratories, FDEP.

9.2. Laboratory Health and Safety Plan.

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

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

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

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

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

9.8. DEP SOP NU-015, Determination of Ammonia in KCl Extracted Sediments using the Lachat QuikChem Autoanalyzer

9.9. DEP SOP NU-019, Determination of Nitrite/Nitrate in KCl Extracted Sediments using the Lachat QuikChem 8000 Autoanalyzer

9.10. DEP SOP CM-011, Gravimetric Analysis: Analytical Weight and Balance Calibration

Appendix of Significant Changes

09/23/2011 References to SOPs were added throughout the document. A cleaning procedure for Ottawa sand was also added.

07/08/2015 Information about creating and completing prep worksheets in the Prep Worksheet Manager module in LIMS was added to Section 6.

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