DETERMINATION OF AMMONIA IN WATER BY GAS DIFFUSION SEGMENTED FLOW ANALYSIS

1. SCOPE AND APPLICATION

1.1. This SOP is applicable to the determination of ammonia in surface, ground, effluents, influents and saline water. The applicable range for this method is from the method detection limit (MDL), 0.002 mg N/L, to 0.20 mg N/L. The range may be extended by dilution. The practical quantitation limit (PQL) is 0.005 mg N/L.

1.2. Tests covered by this SOP are W-NH_3 and W-NH_3-F.

2. SUMMARY OF THE METHOD

2.1. This SOP is based upon EPA Method 350.1, Rev. 2.0 (1993) and OI Analytical Method 327152 utilizing gas diffusion. For method modifications, see Table 3 in the OI Analytical method. For the calibration range, see section 5.3.3 below.

2.2. The sample pH is raised to a pH of >11. The ammonia molecules generated at this pH pass through a gas diffusion membrane and are absorbed into an alkaline hypochlorite solution to form chloramine. The chloramine reacts with salicylate to form indophenol blue in an amount that is proportional to the ammonia concentration. Sodium nitroferricyanide intensifies the blue color. The absorbance is measured at 660 nm.

2.3. Interferences: Heavy metals in the sample may interfere by precipitating. Complexation with citrate should minimize this interference. Samples with background absorbance do not interfere because interferents with color do not diffuse. Samples are filtered prior to analysis.

3. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

3.1. Samples are preserved in the field to a final concentration of 0.2 % (v/v) with H_2SO_4, shipped on ice and stored at $\leq 6\ ^oC$ (not frozen).

3.2. Samples must be analyzed within 28 days of collection date in order for data to be reported unqualified. Samples analyzed more than 28 days after collection date are reported with the Q qualifier.

4. EQUIPMENT AND SUPPLIES

4.1. Instrumentation – OI Analytical Flow Solution® 3100 Automated Chemistry Analyzer for Segmented Flow Analysis.

4.1.1. Precision Pump with 8 channels.

4.1.2. Autosampler 3360.

4.1.3. Expanded Range™ (ER) Photometric Detector with 5 mm path length

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flowcell and 660 nm optical filter.

4.1.4. Heater Module.

4.1.5. Data acquisition system (PC or notebook PC) with WinFLOW™ software, part number 327060 Flow Solution® 3100.

4.1.6. In-line Gas Diffusion Cartridge (PN 327152) and membranes (A001520).

4.1.7. N_2 pillow.

4.1.8. 5510 Branson Sonicator (see Section 5.2.1.).

4.2. Glassware and pipettes (volumetric flasks and measuring cylinders are Class A):

4.2.1. Variable Eppendorf type pipettes (100 µL-1000 µL, 10 µL-100 µL, 1 mL-10 mL)

4.2.2. 100 mL, 200 mL, 500 mL and 1 L volumetric flasks for working standards and reagent preparation.

4.2.3. 1- 4 L container for reagent water.

4.2.4. 1- 1 L amber Nalgene bottle for salicylate reagent.

4.2.5. 3- 1 L Nalgene bottles for complexing agent, startup solution, and 10 N NaOH.

4.2.6. Millipore glass fiber prefilters, cat # APFF04700.

4.2.7. 1- 500 mL bottle for 1M sodium hydroxide solution.

4.2.8. 1- 100 mL and 1- 250 mL graduated cylinder.

4.2.9. Beakers.

4.2.10. Spatulas for weighing out reagents.

4.2.11. 1 L Filtration apparatus.

4.2.12. Disposable culture tubes, borosilicate glass 3x100 mm cat #14-961-27.

4.2.13. Disposable syringes with 0.45 µm filter tips (Whatman Puradisc PP cat. # 05-713-404A).

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

Note: Prior to using the chemicals in this analysis, read their MSDS and the safety notes found in section 9 of this SOP.

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.

Note: All reagent and standard preparations must be documented on the Reagent and Standard logsheet located on the network at: \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\REAGENT_PREP\NH3 This sheet needs to be updated, printed, and submitted as part of the analysis folder.

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Note: Reagent and standard preparations are 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. If available, a Certificate of Analysis for each purchased reagent, standard, and standard reference material is maintained on the Nutrients drive in the \REAGENT_PREP\NH3 folder. All containers holding standards or reagents must be labeled with their unique ID and expiration date.

Note: For the standards prepared daily, a manual version of the unique ID may be created at the time of preparation which is written on the container and manually added to the Reagent and Standard Logsheet in the analysis folder. This form of the unique ID includes the letter N (for NH3 analysis), the concentration, and the date of preparation, which is also the expiration date of the standard; for example, a 0.10 ppm NH3 standard prepared on Sept. 1, 2015 would have the manual ID N0.1020150901.

5.1. Chemicals:

5.1.1. Ammonium Chloride, NH_4Cl

5.1.2. Brij-35, 30 % solution (Ricca cat. #1145)

5.1.3. Sodium citrate dihydrate, $C_6H_8O_7Na_3 \cdot 2H_2O$ (FW 294.1)

5.1.4. Sodium salicylate, $NaC_7H_5O_3$ (FW 160.1)

5.1.5. Sodium Hydroxide, NaOH

5.1.6. Sodium hypochlorite, 8.25 % available chlorine (household bleach, concentration of available chlorine in commercial product can change, see 5.2.7.), NaOCl (FW 74.44)

5.1.7. Sodium Nitroferricyanide (sodium nitroprusside), $Na_2Fe(CN)_5NO*2H_2O$

5.1.8. Sulfuric Acid, concentrated, H_2SO_4

5.1.9. Standard Reference Material (ALTQC) from Environmental Research Associates (ERA).

5.2. Reagents:

5.2.1. **Reagent Water:** DI water or degassed DI water. Degassing is only necessary when air spikes create problems in the detector baseline. Degas DI water using vacuum filtration. The filtration apparatus is setup in a sonicator bath and the filtrate is sonicated for about 15 minutes. After preparing degassed reagent water, store it in a tightly-sealed container to protect it from reabsorbing atmospheric gases.

5.2.2. **Startup solution (1 L):** Add 1.1 mL of 30 % Brij-35 (5.1.2.) to approximately 900 mL of reagent water (5.2.1.) in a 1 L volumetric flask. Make the volume up to the mark with reagent water and mix gently (final concentration 0.03 % Brij-35). Holding time, 14 days

5.2.3. **10 N Sodium Hydroxide Solution (1 L):** While stirring, carefully add 400 g of sodium hydroxide (5.1.5.) to approximately 500 mL of reagent

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water in a 1 L volumetric flask. Allow the solution to cool to room temperature. Make the volume up to the mark with reagent water and mix well. Holding time: 42 days.

5.2.4. **1 M Sodium Hydroxide Solution (500 mL):** Add 50 mL of 10 N Sodium Hydroxide Solution (5.2.3.) to a 500 mL volumetric flask containing 300 mL of reagent water. Dilute with reagent water to the mark and mix well. Holding time, 42 days.

WARNING: Mixing sodium hydroxide with water produces a great of amount of heat. Take appropriate precautions.

5.2.5. **Stock Salicylate/Nitroferricyanide Solution (1 L):** While stirring, carefully add 250 mL of 10 N sodium hydroxide solution (5.2.3.) to approximately 700 mL of reagent (5.2.1.) water in a 1 L volumetric flask. Cool the solution to room temperature. Add 150 g of sodium salicylate (5.1.4.) and 0.3 g of sodium nitroferricyanide (5.1.7.) and stir until dissolved. Dilute to 1 L with reagent water and mix well.

IMPORTANT: Filter solution before use. **Store in an amber PE bottle and refrigerate.** Holding time, 42 days.

Caution: Nitroferricyanide can produce cyanide gas if in contact with acid. Refer to safety section for handling and disposal (9.5.).

5.2.6. **Working Salicylate Reagent (200 mL):** Add 1.4 mL of 30 % Brij-35 solution (5.1.2.) to 200 mL of stock salicylate/nitroferricyanide solution (5.2.5.) and mix gently (final concentration 0.2 % Brij-35). Volume prepared can be adjusted to amount needed for day. Prepare fresh solution daily.

5.2.7. **Working Hypochlorite Solution (1 L):** Add 1 mL of 1 M NaOH (5.2.4) to 800 mL of reagent water (5.2.1.) and mix well. Add sodium hypochlorite (5.1.6.) to a final concentration of 0.01 % (for example, 1.5 mL of 8.25 % available chlorine) to the solution. Dilute to 1 L with reagent water and mix well. Prepare fresh solution daily.

5.2.8. **Complexing Reagent (1 L):** While stirring, add 112 g of sodium citrate (5.1.3.) to 200 mL of reagent water (5.2.1.) in a 1 L volumetric flask. Add 320 mL of 10 N sodium hydroxide solution (5.2.3.) to the mixture. Cool the solution to room temperature. Dilute to 1 L with reagent water and mix well**.** Holding time, 42 days. **IMPORTANT**: Filter solution before use.

5.3. Standards:

5.3.1. **NH_3 stock, 1000 mg N/L:** Dry at least 4 g of NH_4Cl (5.1.1.) for 12-24 hours at 105 ^oC. Dissolve 3.819 g of dried NH_4Cl in 800 mL of DI water contained in a 1 L volumetric flask. Dilute to volume using reagent water (5.2.1.) and invert 12 times. Store under refrigeration. This standard may also be used for TKN analysis (see DEP SOPs NU-081, NU-092, NU-098). Holding time, 180 Days.

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5.3.2. **NH_3 intermediate and spiking solution, 10 mg N/L:** To a 100 mL volumetric flask containing about 50 mL reagent water (5.2.1.), add 1 mL of the 1000 mg N/L NH_3 stock (5.3.1.). Do not acidify. Dilute with reagent water to volume. Store at room temperature. Prepare daily.

5.3.3. **NH_3 working calibration standards, continuing calibration verification (CCV), practical quantitation limit (PQL) standard (PQCK), and blanks (method blank (MBLK) and continuing calibration blank (CCB)):** Prepare standards by pipetting specified amounts of the 10 mg N/L NH_3 intermediate standard (5.3.2.) into volumetric flasks according to the table below. Use reagent water (5.2.1.) to dilute the standards. Invert each standard 12 times, and store at room temperature. Prepare daily.

Standard Concentration (µg N/L)	QC standard	Final Volume (mL)	Volume of conc. H_2SO_4 (µL)	Volume of Intermediate (mL)
200		100	200	2
100	CCV	200	400	2
50		200	400	1.0
20		200	400	0.4
10		200	400	0.2
5	PQCK	200	400	0.1
0	MBLK,CCB	200	400	--

5.3.4. **ALTQC standard (NHXERA):** The supplier for the standard reference material (currently Environmental Resource Associates) differs from the supplier of the calibration standards. This quality control standard (5.1.9) is prepared from the ampule according to the manufacturer's instructions. For the concentration and expiration date of the ampule, see the manufacturer's certificate. The holding time of the prepared stock standard is 180 days. This ALTQC stock solution may be diluted appropriately so that the working concentration falls within the calibration range. The working dilution of the standard is prepared daily. (The X in the designation NHXERA is a digit incremented each time an ampule with a new lot # is used.)

6. SAMPLE ANALYSIS AND QUANTITATION (SEE DEP SOP NU-033)

6.1. Perform any maintenance e.g. replacing pump tubing, membrane, or lamp as needed. Record all maintenance procedures in the instrument maintenance book

6.2. Preparation:

6.2.1. Remove samples from Receiving Room refrigerator and allow them to come to room temperature.

6.2.2. Prepare reagent water (5.2.1.) and reagents as needed. Make sure you

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have at least 3 L of reagent water to start.

6.2.3. Samples with conductivity greater than 5000 µmhos/cm are batched separately. If no conductivity value is given, batch according to the matrix identification in LIMS. Effluents are batched separately.

6.3. Instrument Setup:

6.3.1. Turn on autosampler, pump and detector.

6.3.2. Double-click on the Winflow icon on the computer desktop to start the software.

6.3.3. Clamp down pump tubing (reagents, nitrogen, and debubbler).

6.3.4. Turn on nitrogen pillow, 1 full turn.

6.3.5. Connect **only the salicylate** reagent pump tube to the reagent bottle containing the startup solution (5.2.2.) and the other pump tubes to DI water. Start the pump at 40 % allowing the solutions to flow through the entire system (at least 10 minutes). Connect all three waste lines (sample, reagent, and debubbler) to sink waste reservoir.

6.3.6. The temperature is set at 50 °C. Once the heater reaches 50 °C verify that the baseline is stable.

6.3.7. Make sure that the flowcell is purged of all bubbles and the flow is stable and free from surging. If needed, flicking or pinching the lines helps remove bubbles from flowcell and debubbler.

6.3.8. Leave the salicylate line in the startup solution while connecting all other reagents to their respective bottles allowing them to flow for at least five minutes. Then connect the salicylate line to its reagent bottle and pump the salicylate/nitroferricyanide solution through the system (at least 15 minutes).

6.3.9. When the system has stabilized, run the pump at least 10–15 minutes and verify again that there are no bubbles in the flowcell. Obtain a stable baseline at 660 nm and autozero the baseline before beginning the analysis.

6.3.10. Load the sampler tray with calibrants, blanks, samples, and QC samples.

6.3.11. An LFB (laboratory fortified blank), matrix spike, and a matrix spike duplicate or a sample duplicate must be analyzed for every batch of 10 samples. Add 50 µL of 10 mg N/L spiking solution (5.3.2.) to 10 mL of sample and blank (5.3.3.) for a 0.050 mg N/L spike.

6.3.12. A filtered method blank (MBLK_F, 5.3.3.) must be poured with every batch of samples.

6.3.13. Start and finish every run with a CCB (5.3.3.) and a CCV (5.3.3.). After these initial standards add your PQCK (5.3.3.) and ALTQC (5.3.4.). Analyze a CCB (5.3.3.) and a CCV (5.3.3.) every 10 cups throughout the entire run.

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6.4. Analysis setup in the Winflow program:

6.4.1. Click on the box called sample table located in the center of the screen. It will show the last table used.

6.4.2. On the menu bar: select 'File' and 'open'. Select the Nutrients drive from the drop down box, then the OI Analytical folder, then the NH3 subfolder. Then, select: Template.TBL. This template includes the setup for the weighted linear calibration. All standards are prepared manually as described in 5.3.3., and are analyzed in triplicate.

6.4.3. Start with cup 101 and enter sample ID's in the 'Name' column. For the 'Type' column, enter U for samples and RB's for baseline corrections. Type RB's after every ten cups.

A typical run sequence includes:

Sync – high standard (5.3.3.)
Blank – to check for carryover (5.3.3.)
Calibrants – run in triplicate (5.3.3.)
CCV/CCB – these checks are run every ten cups (5.3.3.) and at the end of the run
PQCK (5.3.3.)
NHXERA_(dilution factor) – (5.3.4.) the SRM is diluted within the calibration range
Batched samples, including an MBLK_F, an LFB, and a set of duplicate spikes per batch

6.4.4. Save the template as YYMMDDN#.TBL (e.g. 140919N1.TBL), where N indicates an ammonia analysis on SFA Instrument 1 (use H for an ammonia analysis on SFA Instrument 2) and # indicates the run number for the day. The file should be saved on the Nutrients drive at \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\OI-Analytical\NH3\ in the current year's sub-folder.

6.4.5. Go to 'File' and select 'print' to obtain the benchsheet. Close the sample table box.

6.5 Start the analytical run:

6.5.1. Click on the box called 'Collect Data' located in the center of the screen.

6.5.2. Enter your initials for 'Operator Name' and 'Operator ID' and select OK.

6.5.3. In the 'Run Setup' box check that your sample table name and your method are correct and select OK.

6.5.4. Specify the file name for the results report. Name the file using the same convention as for the sample table (6.4.4.) (e.g. YYMMDDN#.RST)

6.5.5. Click on the play button to view your baseline. Check for bubbles in the flow cell (see 6.3.7.). After your baseline is stable, zero it out (6.3.9.).

6.5.6. Start the run by clicking on the fast forward button.

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6.5.7. After the run is finished print the peak table, calibration, and the peak plot. To print the run report go to 'view' in the menu bar, select 'reports', and print report 'by peak'.

6.5.8. To export data to QC Manager, go to File > Export Report, and save the upload file as YYMMDDN#.txt in the current year's subfolder located at \\FLDEP1\DEAR\Labs\lab3\Chem_Data\Inorganic\Nutrients\OI-Analytical\NH3\.

6.6. Quantitation/Calculations:

6.6.1. The instrument reports results for Ammonia analysis in ppb. The results are converted to mg N/L when uploaded into the QC Manager program.

6.6.2. 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 Quality Manual.

6.6.3. The working calibration standards are prepared according to section 5.3.3. The correlation coefficient for the weighted linear calibration is calculated by the instrument software. Recoveries for the calibrants are calculated according to Section 5.9 of the FDEP Quality Manual.

7. DATA ARCHIVAL

7.1. 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(s) (W-NH3, W-NH3-F), filename/s (YYMMDDN# or YYMMDDH# (where N is for SFA 1, H is for SFA 2, and the # indicates the 1st, 2nd etc. run of the day), and initials of the analyst.

7.2. Each report folder should contain the following items - the run report(s), bench sheet(s), Reagent and Standard Logsheet, the backlog containing the batching documentation, and a copy of the data and QC assessments uploaded from QC Manager to LIMS at the time of test authorization.

7.3. 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.

7.4. OI SFA instrument *.TBL run table files, *.RST raw data files, and text data transfer files for upload to QC manager are stored in electronic format in the current year's subfolder located at \\FLDEP1\DEAR\Labs\lab3\Chem_Data\Inorganic\Nutrients\OI-Analytical\NH3\.

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7.5. Method validation data is on file with the supervisor. Digital copy is also stored on the network, under an appropriate sub-folder in \\fldep1\dear\Labs\Lab5\Chemistry\Inorganic\Nutrient\Validations.

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

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

8.2. A continuing calibration verification, CCV (5.3.3.) and a CCB (5.3.3.) are run every 10 cups and at the beginning and end of each run. An MBLK is analyzed for every batch of 10 samples. Acceptance limits for the recoveries of the check standard are 90-110 %. Acceptance limits for the CCB's and MBLK's are < 0.002 and > -0.002 mg N/L.

8.3. One certified standard reference material, ALTQC (5.3.4.), is analyzed on every analytical run. The supplier for the QC stock standard differs from the supplier of the calibration standards. Acceptance limits for the recovery of the ALTQC are 90-110 %.

8.4. One practical quantitation limit level standard, PQCK (5.3.3.), is analyzed on every analytical run. Acceptance limits for the recovery of the PQCK standard are 70-130 %. The PQL also serves as the spike for the ongoing MDL and PQL verification.

8.5. An LFB, a matrix spike, and a matrix spike duplicate or a sample in duplicate should be analyzed for every batch of 10 samples. Acceptance limits for the recoveries of the LFB's and matrix spikes are 90-110 %. The sample/matrix spike reproducibility should be less than 20 % RPD for results over the practical quantitation limit (PQL).

8.6. Linear Calibration Range (LCR): See the FDEP Quality Manual Appendix B, Section 7.0, 'Protocol for Determining the Test Method Range of Applicability'. The correlation coefficient of the weighted linear calibration must be equal to or larger than 0.995. Recoveries for calibration standards above the PQL must be 90-110 %. These calculations are conducted manually by the analyst and recorded on the analysis printout.

8.7. Every day samples are analyzed a new calibration must be performed at the beginning of the analysis and the LCR must be verified (see 8.6.). Consecutive runs on one day may use the same calibration.

9. SAFETY/HAZARDOUS WASTE MANAGEMENT/POLLUTION PREVENTION

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

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

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samples and reagents.

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

9.4. The instrument waste is collected in a container labeled 'Sink Waste' and disposed of down the sink whilst flushing with water.

9.5. The sodium nitroferricyanide (5.1.7.) used to prepare the stock salicylate/nitroferricyanide solution (5.2.5.) produces cyanide gas if it encounters acid. Wear all personal PPE when preparing and thoroughly rinse flasks and containers after acid washing. Dispose excess sodium nitroprusside crystals by lab packing. Excess color reagent can be disposed of down the sink when flushed thoroughly with water.

10. REFERENCES/DEFINITIONS

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.

10.1. EPA method 350.1, Rev. 2.0 (1993).

10.2. OI Analytical Method 327152 and User Manuals.

10.3. Quality Manual, Bureau of Laboratories, FDEP.

10.4. Laboratory Health and Safety Plan.

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

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

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

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

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

10.10. DEP SOP NU-081, Determination of Total Kjeldahl Nitrogen in Soils Using the Westco SmartChem Discrete Analyzer.

10.11. DEP SOP NU-092, Determination of Total Kjeldahl Nitrogen in Water Using the Seal AQ2 Discrete Analyzer.

10.12. DEP SOP NU-098, Determination of Total Kjeldahl Nitrogen in Water by Gas Diffusion Segmented Flow Analysis.

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

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Appendix of Significant Changes

07/01/2013 Reagent water degassing was made optional in section 5.2.1.

10/31/2013 Documentation protocol for standards prepared daily was modified in section. See note at the start of section 5.

04/01/2014 Started use of 30 % Brij solution (from Ricca) instead of 21 % (from OI Analytical). Final Brij concentration was not changed.

10/07/2015 Data archival information was clarified in Section 7.

12/10/2019 Section 6 sample matrix batching and data exporting was clarified. Section 8 the PQL level standard serves as the spike for the ongoing MDL and PQL verification data collection. Section 9 safety and waste disposal procedure was updated.

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