

SOP-C-104

**Determination of Ammonia
as Nitrogen**

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Laboratory Manager

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Date



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Texas Institute for Applied Environmental Research

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- i. Identification of the method**
 - a. Standard Methods online 4500-NH₃ G (approved 2017)
 - b. Modifications:
 - i. Standards are kept at the same holding time as samples and not made fresh daily.
 - ii. Preservation temperature meets TNI requirements.
 - iii. Solid phenol is used instead of liquid phenol.
 - iv. Lachat method allows for range of 0.02-4.0 mg/L and does not require distillation.
- ii. Applicable matrix or matrices**
 - a. Non-potable water or aqueous extracts.
 - b. Solids and drinking water may be analyzed, but these are not TNI accredited matrices at TIAER.
- iii. Limits of detection and quantitation**
 - a. 0.02 LOD to 4.0 mg/L ammonia as nitrogen. LODs are determined annually. Concentration or dilution may extend the range.
- iv. Scope and application, including parameters to be analyzed**
 - a. Ammonia nitrogen in nonpotable water.
- v. Summary of the method**
 - a. Spectrophotometric analysis of water samples upon color development from addition of reagent.
- vi. Definitions**
 - a. EDTA- disodium ethylenediamine tetraacetate, disodium salt.
 - b. Standard QA/QC definitions are found in QAM-Q-101, "Laboratory Quality Control".
 - c. Instrument component names and start up solutions are described in QAM-I-102, "Operation and Calibration of the Autoanalyzers."
- vii. Interferences**
 - a. Intensity of color is pH-dependent.

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- b. Calcium and magnesium in sufficient concentrations can precipitate during analysis.
- c. Turbidity is removed by filtering the sample.

viii. Safety

- a. Alkaline phenol is harmful if inhaled, swallowed or absorbed through the skin and may cause burns. Gloves are worn when handling. Contacted skin is washed with copious amounts of water.
- b. Sodium nitroferricyanide is extremely toxic and liberates poisonous gas when in contact with acid. A respirator, rubber gloves, protective clothing and appropriate ventilation (preferably a hood) are used as needed. Gloves are washed thoroughly before removing.

ix. Equipment and supplies

- a. Refer to QAM-I-102, "Operation and Calibration of the Autoanalyzers".
- b. Balance capable of accurately weighing to the nearest 0.01 g.
- c. Assorted glassware, Class A.

x. Reagents and standards

- a. Deionized water (DI): precautions must be taken to ensure that the water remains ammonia free. Use fresh DI when possible or keep the container tightly closed and away from ammonia sources.
- b. Sampler Wash Solution (DI): If the samples are preserved with sulfuric acid, acidify DI in equal proportions to match sample pH <2. Add 2 mL H₂SO₄ per liter of DI.
- c. Manifold Solution for FIA: Use DI water.
- d. Stock Complexing Reagent (5% EDTA) (1 L): Dissolve 50g of EDTA (disodium salt) in 800 ml of DI. Add 9 grams of NaOH. Stir until all dissolved. Dilute to 1 liter.
- e. Sodium nitroferricyanide (0.05% Sodium nitroprusside) (1 L): Dissolve 0.5g of sodium nitroferricyanide in 1 L of DI. Store this solution in an amber bottle at room temperature.
- f. Alkaline phenol (1 L): Using a 1 L volumetric flask, cautiously add, with stirring, 32 g of NaOH to

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approximately 700 mL DI. When solution is cool, slowly add 83 g phenol in small quantities. Dilute solution to 1 L and mix well. The resulting solution is a light straw color. Store the reagent in an amber bottle and refrigerate. Stability is approximately one month, but discard if the solution becomes dark amber in color.

- g. Sodium hypochlorite solution (500 mL): Dilute 220 mL of a bleach solution containing 6.0% NaOCl (such as Clorox™) to 500 mL with DI. Mix well and transfer to an amber bottle. Available chlorine level is approximately 2.5%. Since Clorox™ is a proprietary product; its formulation is subject to change. The analyst must remain alert to detecting any variation in this product significant to its use in this procedure. This reagent is not stable and is prepared fresh daily.
- h. Stock solution (1000 mg/L): Dissolve 3.819 g of ACS grade anhydrous ammonium chloride, (NH₄Cl dried at 105° C), in DI and dilute to 1 L in a volumetric flask. Refrigerate solution when not in use. 1.0 mL=1.0 mg NH₃-N. Commercial standards are used.
- i. Working solution, WS, (100 mg/L): Dilute 100.0 mL of stock solution to 1000 mL in a volumetric flask with DI. 1.0 mL = 0.1 mg NH₃-N. Commercial standards are used.
- j. Calibration (CAL) standards: Using the working solution WS, prepare the following suggested calibration standards in DI in 100 mL volumetric flasks and acidify to same level as samples: NH₃-N, mg/L: 0.06 (LOQcal), 0.1, 0.2, 0.5, 1.0, 2.0, and 4.0. Standards are good for 28 days from the date of preparation if preserved.
- k. Laboratory Control Standard (LCS) stock solution (1000 mg/L)- prepare as specified by the Laboratory Manager from raw materials (such as a different lot of ammonium chloride) or purchased from a commercial source.
- l. Prepare a 2.0 mg/L LCS/LCSD/ICV/CCV standard by diluting 1.0 mL of LCS stock solution to 500 mL in a volumetric flask and acidifying. This can also be obtained commercially. This standard may also contain nitrate/nitrite nitrogen mixed in for the LCS/LCSD in that analysis. The LCS/LCSD and ICV/CCV are analyzed as separate standards from this solution.

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m. Prepare a 0.06 mg/L LOQcv standard (calibration verification) from a separate source stock than the calibration standards by dilution with DI into another flask. Acid preserve in the same manner as other standards.

xi. Sample collection, preservation, shipment and storage

- a. Holding Time: 28 days.
- b. Preservation: Refrigerate sample to >0 to $\leq 6^{\circ}\text{C}$, filter before acidification (if needed) for dissolved analyte.
- c. The TIAER Lab does not collect or normally ship samples for this analyses.
- d. For dissolved ammonia as nitrogen, grab samples are normally field filtered and preserved in accordance with field protocols.
- e. For total ammonia, sample is acid preserved, then filtered immediately prior to analysis to protect from instrument damage by suspended matter.
- f. If not field filtered and preserved, filter samples in the laboratory through 0.45 μm filter membrane filters in accordance with QAM-Q-111, "Aliquot Preparation and Sample Preservation".
- g. Analyze samples not preserved with acid within 48 hours of collection.
- h. Preserve samples to pH <2 with concentrated H_2SO_4 (about 3 drops of conc. H_2SO_4 to 50 mL for most samples) and store at >0 - $\leq 6^{\circ}\text{C}$.
- i. Analyze preserved samples within 28 days of collection.

xii. Quality control

- a. All aspects of this procedure comply with QAM-Q-101, "Laboratory Quality Control".

xiii. Calibration and standardization

- a. Use calibration standards to establish the standard curve. Analyze an ICV and IBV immediately after calibration. Refer to the Procedure section below and QAM-I-102, "Operation and Calibration of the Autoanalyzers".

xiv. Procedure

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- a. Refer to QAM-I-102, "Operation and Calibration of the Autoanalyzers".
 - b. Refer to the ammonia nitrogen flow diagram in the QuikChem Methods Manual for FIA manifold setup.
 - c. Parameter settings can also be found in these references.
 - d. Make the calibration standards as described. Record these standards in the Standard Log. The AWRL/LOQ is placed as the lowest calibration standard at the beginning of an analytical run once each day samples are analyzed (ARB) and passes acceptance criteria.
 - e. Create a sample table as specified in QAM-I-102. Use the NH₃ template nh3g for FIA.
 - f. Use calibration standards to establish the standard curve. Analyze an ICV and IBV immediately after calibration.
 - g. Use the 2.0 mg/L standard made from a source other than calibration standards as the ICV, CCV, LCS and LCSD. The LCS and LCSD are analyzed with every preparation batch of twenty or less samples (PB). Parameter settings in the template/tray direct the instrument to perform this automatically.
 - h. Analyze a CCV and CCB, sample duplicate and spike every run batch of 10 samples or less (QCB), spike duplicate and LCS/LCSD at least every 20 samples (PB).
 - i. Spiking is done using 10 mL of sample and 0.01 mL of the 1000 mg/L stock standard, or a proportional equivalent thereof. Record how it is made in the log.
 - j. Load sample tray according to the sample table printout.
- xv. Data analysis and calculations;**
- a. For data handling, See QAM-I-102, "Operation and Calibration of Autoanalyzers", for calculation of data.
 - b. Review the graphic display of the output and identify, correct or resolve any anomalies (i.e. missed or mismarked peaks).
 - c. Enter data into the LIMS and review the QC evaluation.
 - d. Reanalyze if necessary.
 - e. Print a copy of the reviewed spreadsheet showing concentration of samples for placement in the personal logbook.

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- f. All data are documented and maintained in accordance with QAM-A-102, "Document and Data Control".
- g. The baseline is within \pm the LOQ value for the method.
- h. All dilution procedures are described in detail.

xvi. Method performance

- a. Method performance: refer to QAM-Q-101, "Laboratory Quality Control"

xvii. Pollution prevention

- a. Pollution prevention: refer to QAM-W-101, "Disposal of Laboratory Waste"

xviii. Data assessment and acceptance criteria for quality control measures

- a. Data assessment and acceptance: refer to QAM-Q-101, "Laboratory Quality Control"

xix. Corrective actions for out-of-control data

- a. Corrective action: refer to QAM-Q-105, "Corrective Actions"

xx. Contingencies for handling out-of-control or unacceptable data

- a. refer to QAM-Q-101, "Laboratory Quality Control" and QAM-Q-105

xxi. Waste management

- a. Waste management: refer to QAM-W-101, "Disposal of Laboratory Waste"

xxii. References

- a. QuikChem Methods Manual, LaChat Instruments, Inc., 2000.
- b. Standard Methods for the Examination of Water and Wastewater, latest online Edition (approved 2017), ed. by Arnold E. Greenberg, et al., APHA, AWWA, Washington D.C., Method 4500-NH₃ G-97.
- c. The National Environmental Laboratory Accreditation Conference Institute (TNI) standard, 2016.

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xxiii. Any tables, diagrams, flowcharts and validation data
none

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