

FERTILIZER METHODS

Chapter

NITROGEN ANALYSIS

Subject

Ammoniacal Nitrogen (Improved) –
Flow Injection

Adapted from QuickChem Method 14-107-06-2-C

By: Lachat Instruments 6645 West Mill Road, Milwaukee, WI 53218

Determination of Ammonia in Fertilizers by Flow Injection Analysis

4 to 600 mg N/L as NH₄

0.1 to 15.0 % N/1 g sample

PRINCIPLE

This is a low flow method, which measures ammonia. When ammonia is heated with salicylate and hypochlorite in an alkaline phosphate buffer, a colored compound is produced. The absorbance of the compound at 660 nm is directly proportional to the ammonia concentration. The color is intensified by the addition of sodium nitroprusside. The method detection limit is 1 mg NH₄ N/L.

SCOPE & APPLICATION

This method covers the determination of ammonia in fertilizer samples prepared using FM-430 or FM-701, but may also be used with appropriate calculations to determine percent nitrogen in Kjeldahl and Block digestions of fertilizer samples. The applicable range is 4 to 600 mg NH₄ N/L. The method detection limit is 1 mg NH₄ N/L. The method throughput is 40 injections per hour. **Note: This method is intended for use with methods FM-451 & FM-462, but may be used alone.**

DEFINITIONS

See: BUREAU OF FEED, SEED & FERTILIZER LABORATORIES, STANDARD OPERATING PROCEDURES, and LACHAT DEFINITIONS

INTERFERENCES

Non-volatile amines such as cysteine, ethanolamine and ethylenediamine may cause a decrease in ammonia sensitivity.

SAFETY

Each laboratory is responsible for maintaining a current awareness file of the Occupational Health and Safety Act (OSHA) regulations regarding the safe handling of the chemicals

specified in this method. A reference file of Material Safety Data Sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.

EQUIPMENT & SUPPLIES

Balance - analytical, capable of accurately weighing to the nearest 0.0001 g.

Glassware - Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass containers.

Flow injection analysis equipment designed to deliver and react sample and reagents in the required order and ratios.

Auto-Sampler

Multichannel proportioning pump

Reaction unit or manifold

Colorimetric detector

Data system

Heating unit

1 mm flow cell (Lachat Part No. 24950)

PVC Pump tubes **NOTE: PVC PUMP TUBES MUST BE USED FOR THIS METHOD.**

REAGENTS AND STANDARDS

PREPARATION OF REAGENTS

Use deionized (D.I.) water (10 megohm) for all solutions.

Degassing with helium:

To prevent bubble formation, degas all solutions except the standards with helium. Use He at 140kPa (20 lb/in²) through a helium degassing tube (Lachat Part No. 50100.) Bubble He through the solution for one minute.

Reagent 1. Buffer Solution

By Volume: In a 1 L volumetric flask, dissolve **20 g sodium hydroxide** (NaOH), **42 g sodium phosphate heptahydrate** (Na₂HPO₄·7H₂O), and **50 g potassium sodium tartrate tetrahydrate** (Na₂HPO₄·7H₂O), in **600 mL D.I. water**. Dilute to mark with **D.I. water** and stir to dissolve.

Reagent 2. Nitroprusside/Salicylate Color Reagent

By Volume: In a 1 L volumetric flask, dissolve **150 g sodium salicylate**, **1.0 g sodium nitroprusside** and **0.4 g Brij-35** (C₁₂H₂₅(OCH₂CH₂)₂₃OH) in about **700 mL D.I. water**. Dilute to mark with **D.I. water** and stir until dissolved. (Brij-35 is a registered trademark of ICI Americas, Inc.)

Reagent 3. Hypochlorite Solution

By Volume: In a **500 mL** volumetric flask, dilute **30 mL 5.25% sodium hypochlorite** in **400 mL D.I. water**. Dilute to mark with **D.I. water** and invert to mix. Prepare daily.

PREPARATION OF STANDARDS

To prepare the stock and working standards, the following containers will be required:

By Volume: One 1 L and five 500 mL volumetric flasks.

By Weight: One 1 L and five 500 mL containers.

Standard 1. Stock Standard 1000 mg NH₄N/L

By Volume: In a 1 L volumetric flask dissolve **4.750 ammonium sulfate** (reagent grade) in approximately **900 mL D.I. water**. Dilute to the mark with **D.I. water** and invert to mix.

Working Standards (Prepare Daily)	A	B	C	D	E
Concentration mg NH ₃ -N/L	600	300	150	60	0.0

By Volume

Volume (mL) of stock standard 1 diluted to 500 mL with DI water	300	150	75	30	---
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By Weight

Weight (g) of stock standard 1 diluted to final weight (~500g) divided by factor below with DI water	300	150	75	30	---
Division Factor	0.6	0.3	0.15	0.06	---
Divide exact weight of the standard by this factor to give the final weight					

SAMPLE PRESERVATION AND STORAGE

If the sample contains particulate matter, it must be filtered through at least a Whatman # 4 or equivalent filter to avoid plugging the valve or manifold. Once the sample has been filtered, it should be allowed to settle for about 5 minutes before analysis.

To further decrease the chance that particulate matter will be aspirated with the sample, set the probe so that there is about ½ inch of clearance from the bottom of the sample tube.

The diluted samples should be analyzed as soon as possible. If they cannot be analyzed immediately, they should be refrigerated.

CALIBRATION PROCEDURE

Pump D.I. water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.

Place samples and/or standards in the sampler. Input the information required by the data system, such as concentration, replicates and QuikChem scheme (See **DATA ANALYSIS AND CALCULATIONS**).

Calibrate the instrument by injecting the standards. The data system will then associate the concentrations with the instrument responses for each standard.

SYSTEM NOTES

For information on system maintenance and troubleshooting refer to the Troubleshooting Guide in the System Operation Manual.

Let reagents run for 10-15 minutes prior to starting analysis. The heater must be at 60°C before beginning.

This method can be run with a second order calibration if desired. However, this will lead to less accurate results.

Use consumer bleaches with caution. Proprietary additives may contribute to staining of tubing and data quality.

Add reagents in the order that they appear on the manifold to reduce staining.

DATA ANALYSIS AND CALCULATIONS

Calibration is performed by injecting standards. The data system will then prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation.

Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

Report results in % N as NH₄ in fertilizer.

METHOD PERFORMANCE

See: Quikchem method 14-107-06-2-C from Lachat Instruments.

FLOWCHARTS AND VALIDATION DATA

See: Quikchem method 14-107-06-2-C from Lachat Instruments.

TABLES AND DIAGRAMS

DATA SYSTEM PARAMETERS FOR QUIKCHEM 8000

The timing values listed below are approximate and will need to be optimized using graphical events programming.

Sample throughput: 40 samples/h, 90 s/sample
 Pump Speed: 35
 Cycle Period: 90 seconds.

Analyte Data:

Concentration Units: mg NH₄ N/L
 Peak Base Width: 47 s
 % Width Tolerance: 100
 Threshold: 37700
 Inject to Peak Start: 85 s
 Chemistry: Direct

Calibration Data:

Level	1	2	3	4	5
Concentration mg NH ₃ -N/L	600	300	150	60	0.0

Calibration Rep Handling: Average
 Calibration Fit Type: 3rd Order Polynomial
 Weighting Method: None
 Force through zero: No

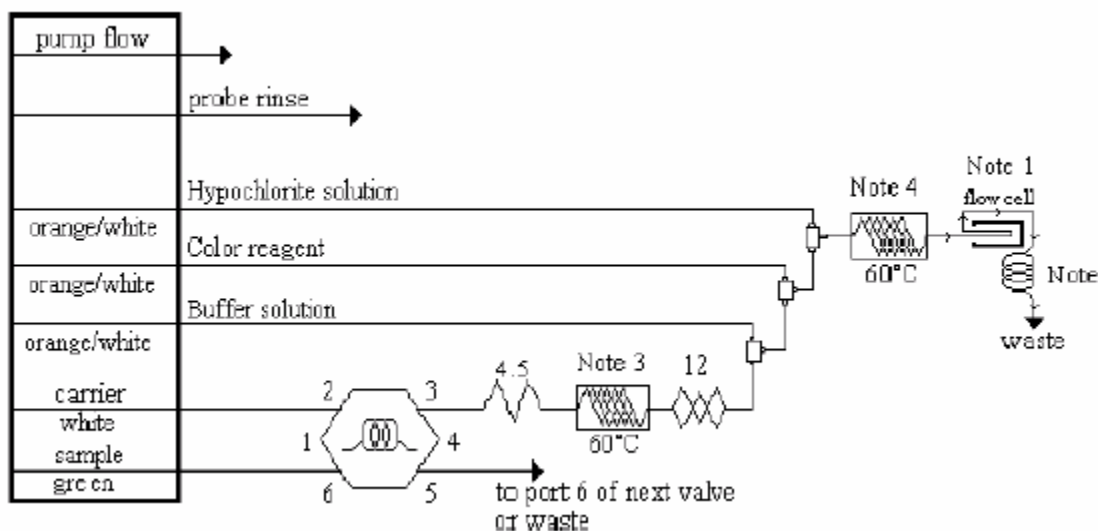
Sampler Timing:

Min. Probe in Wash Period: 20 s
 Probe in Sample Period: 35 s

Valve Timing:

Load Time: 0 s
 Load Period: 25 s
 Inject Period: 65 s

AMMONIA MANIFOLD DIAGRAM



Carrier: D.I. water
Manifold Tubing: 0.5 mm (0.022 in) i.d. This is 5.2 µL/cm.
QC8000 Sample Loop: 13 cm
Interference Filter: 660 nm
Apparatus: An injection valve, a 1 mm path length flow cell, and a colorimetric detector module is required
4.5: 70 cm of tubing on a 4.5 cm coil support
12: 255 cm of tubing on a 12 cm alternating coil support
Note 1: The flow cell is 1 mm path length.
Note 2: 50 cm back pressure loop, 0.52 mm (0.022 in) i.d.
Note 3: 175 cm of tubing on the heater block.
Note 4: 650 cm of tubing on the heater block.
Note 5: The same heating module is used for both (see notes 3 and 4) heaters.

Note 6: PVC PUMP TUBES MUST BE USED FOR THIS METHOD

APPROVAL:

Approved by: Leigh Humphreys Date: 1/27/03
Signature

Bureau Chief
Title

METHOD REVISION HISTORY:

Version	Date	Description	Author
Original	9/27/96	Replaces N-400.30	W.M. Bell
Original	6/11/98	Replaces N-410.00	W.M. Bell
Original	6/30/98	Replaces FM-455	W.M. Bell
Original	1/27/03	Replaces FM-470	W.M. Bell

REFERENCE:

U.S. Environmental Protection Agency, Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Revised March 1983.

Quikchem method 14-107-06-2-C from Lachat Instruments.