Ammonium Nitrogen (DIN 38406)

(P/N 000857 and P/N 000858)

A. Scope and Application

This method is used for the determination of ammonium nitrogen in various types of waters (such as ground, drinking, surface, and waste waters). The applicable range of this method is 0.1-10.0mg/L N. The range of application may be adapted by varying the operating conditions.

B. Summary of Method

In a continuously flowing gas segmented carrier stream, ammonium present in the sample reacts in alkaline solution with hypochlorite, which has previously been liberated from dichloroisocyanurate. The chloramine formed reacts under catalysis of nitroprusside with salicylate at a temperature of 37°C to form a blue-green indophenol dye which is quantitatively measured at 640nm[1-4].

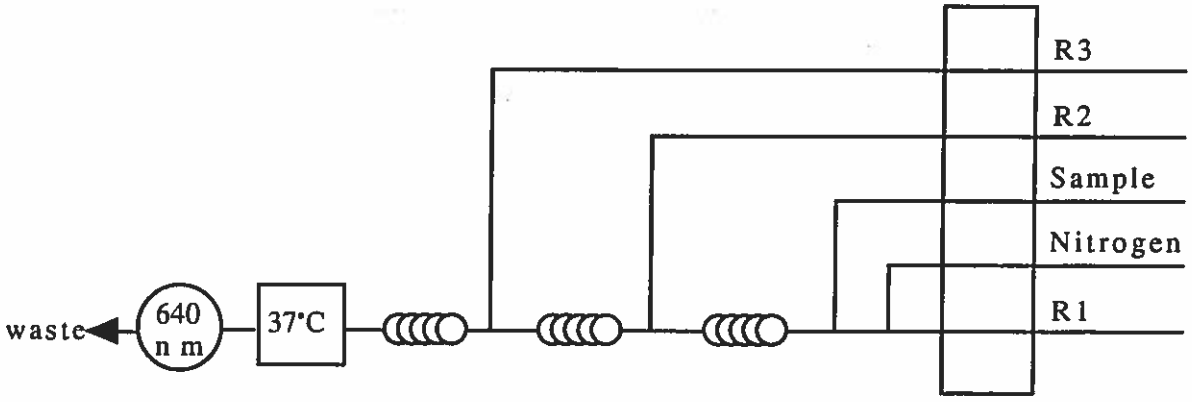
C. Interferences

Low-molecular weight amines react similarly to ammonia and will consequently lead to erroneously high results. Interferences may occur if the sample, mixed with the alkaline solution, does not reach a pH of at least 12.5. This mainly happens with strong acidic and buffered samples. Metal ions in high concentrations, which tend to precipitate as hydroxides, cause poor reproducibility. Removal of interfering organic material can be accomplished by filtering the sample through activated charcoal, provided a change of the ammonium content in the sample can be ruled out when this approach is used.

D. Performance Specifications

Range:	0.1-10mg/L N
Rate:	48 samples/hr.
Carryover:	0.04%
Precision (0.4mg/L):	0.1.5%
Precision (1.6mg/L):	0.90%
Method Detection Limit:	0.05mg/L N

E. Generalized Flow Diagram



F. Sample Handling and Preservation

Containers of glass, polyalkylenes and polytetrafluoroethylene (PTFE) are suitable for sample collection. All containers coming in contact with the sample should be thoroughly cleaned with hydrochloric acid (1N) and should also be rinsed several times with water. Analyze samples immediately after collection. Alternatively, add sulfuric acid (2mL/L) to adjust a pH of approximately 2, store at 2-5°C in the dark and analyze within the next 24 hours. In exceptional cases, and after acidification, the sample may be stored up to 2 weeks, provided the sample has been membrane-filtered. The applicability of this preservation procedure should be checked for each individual case of examination.

G. Raw Materials Required

NOTE: *Chemicals should be of ACS grade or equivalent.*

Ammonium Chloride, NH_4Cl (FW 53.49)
Polyoxyethylene lauryl ether (23)
Deionized Water (ASTM Type I or II)
Sodium Dichloroisocyanurate $NaC_3Cl_2N_3O_3$ (FW 219.95)
Sodium Hydroxide NaOH (FW 40.00)
Sodium Nitroprusside Dihydrate $Na_2[Fe(CN)_5NO]\cdot 2H_20$ (FW 297.97)
Sodium Salicylate, $NaC_7H_5O_3$ (FW 160.11)
Trisodium Citrate Dihydrate, $Na_3C_6H_5O_7\cdot 2H_20$ (FW 294.10)

H. Reagent Preparation

NOTE: *For best results, filter all reagents prior to use.*

1. Citrate Buffer Solution (reagent solution R_1) (1L)

Trisodium Citrate Dihydrate.....40g
$Na_3C_6H_5O_7 \cdot 2H_2O$ (FW 294.10)
Brij-35, 30% Solution 2mL
Deionized Water

Dissolve 40g of trisodium citrate dihydrate in approximately 600mL of deionized water contained in a 1L volumetric flask. Add 2mL of Brij-35, 30% solution and dilute to volume with water. Mix well. The solution can be stored cooled in a brown-glass bottle for 1 week.

2. Sodium Salicylate Solution (reagent solution R_2) (1L)

Sodium Salicylate.....34g
$NaC_7H_5O_3$ (FW 160.11)
Sodium Nitroprusside Dihydrate.....0.4g
$Na_2[Fe(CN)_5NO] \cdot 2H_2O$ (FW 297.97)
Brij-35, 30% Solution 1mL
Deionized Water

Dissolve 34g of sodium salicylate and 0.4g of sodium nitroprusside dihydrate in approximately 600mL of deionized water contained in a 1L volumetric flask. Add 1mL of Brij-35, 30% solution and dilute to 1L with deionized water. This solution can be stored cooled in a brown-glass bottle for 1 week.

3. Sodium Hydroxide Solution, 5M (500mL)

Sodium Hydroxide..... 100g
NaOH FW (40.00)
Deionized Water

Carefully add with stirring 200g of sodium hydroxide to approximately 250mL of deionized water contained in a 500mL volumetric flask. Cool to room temperature. Dilute to volume with deionized water, and mix well.

4. DIC Solution (reagent solution R_3) (1L)

Sodium Dichloroisocyanurate.....0.8g
$NaC_3Cl_2N_3O_3$ (FW 219.95)
5M Sodium Hydroxide Solution.....50mL
Deionized Water

Add 50mL of 5M sodium hydroxide solution to approximately 600mL of deionized water contained in a 1L volumetric flask. Dissolve 0.8g of sodium dichloroisocyanurate in this solution and dilute to 1L with deionized water. Prepare this reagent fresh before use.

5. Startup Solution(1L)

Brij-35, 30% w/v.....2mL
Deionized Water

Add 2mL of Brij-35 to approximately 800mL deionized water contained in a 1L flask. Mix gently. Dilute to volume with deionized water.

I. Calibrants

1. Stock Ammonium Calibrant 1000mg/L as N (1L)

Ammonium chloride, dried at 105°C.....3.819g
NH_4Cl (FW 53.49)
Deionized Water

Dissolve 3.819g of ammonium chloride in approximately 900mL of deionized water contained in a 1L volumetric flask. Dilute the solution to 1000mL with deionized water. Mix well. This solution may be stored in a refrigerator for at least 3 months.

2. Intermediate Ammonium Calibrant 100mg/L as N (100mL)

Use a volumetric pipet to add 10mL of Stock Calibrant to approximately 80mL of deionized water contained in a 100mL volumetric flask. Dilute the solution to 100mL with deionized and mix well. This solution may be stored in a refrigerator for at least 1 week.

3. Working Calibrants (100mL)

Working calibrants may be prepared to cover the desired range by adding the appropriate volumes of stock (or intermediate) calibrant to 100mL volumetric flasks that contain approximately 80mL of deionized water. Dilute the solution to 100mL with deionized water and mix well.

The following formula can be used to calculate the amount of stock (or intermediate) calibrant to be used.

$$C_1V_1 = C_2V_2$$

where:

C_1 = desired concentration (in mg/L) of working calibrant to be prepared

V_1 = final volume (in mL) of working calibrant to be prepared (generally 100mL)

C_2 = concentration (in mg/L) of stock (or intermediate) calibrant

V_2 = volume (in mL) of stock (or intermediate) calibrant to be used

Rearranging the equation to solve for V_2 yields:

$$V_2 = \frac{C_1V_1}{C_2}$$

For example, to prepare a 1.0mg/L working calibrant from a 1000mg/L stock calibrant, use 0.1mL (100µL) of the stock calibrant in 100mL final volume.

$$V_2 = \frac{(1.0\text{mg/L})\ (100\text{mL})}{1000\text{mg/L}}$$

$$V_2 = 0.1\text{mL}$$

Add this amount of stock calibrant to the volumetric flask and then dilute to volume with the sampler wash solution.

Standard curves in desired ranges can be derived from the formula above or table below.

Range 1.0-10.0mg/L as N

Nominal Concentration (mg/L)	Intermed. Cal. Vol. (mL)
1.0	1.00
2.0	2.00
4.0	4.00
6.0	6.00
8.0	8.00
10.0	10.00

Range 0.10-1.0mg/L as N

Nominal Concentration (mg/L)	Intermed. Cal. Vol. (µL)
0.10	100
0.20	200
0.40	400
0.60	600
0.80	800
1.00	1,000

J. Operating Procedure

1. Set up the cartridge shown in the flow diagram.
2. Turn power on to all units. Select a temperature of 37°C for the heater unit to be used.
3. Begin pump flow with start-up solution. Let the system run for about 5-10 minutes to establish a stable baseline.
4. Place the reagent lines into the appropriate containers and allow at least 10 minutes for the system to stabilize before calibrating or autozeroing the detector.
5. Load the sampler tray with calibrants, blanks, samples, and QC samples.
6. Select the appropriate parameters for the computer, detector, and sampler. (See " Method Parameters" at end of methodology.)
7. Begin analysis.

K. Operating Notes

1. Prepare ammonia-free water by passing distilled water through a mixture of strongly acidic cation and strongly basic anion exchange resins[3].
2. To prevent ammonia contamination from air, segment the analytical stream with nitrogen or draw air through a 5N sulfuric acid solution.

L. References

1. German Standard Methods for the Examination of Water, Wastewater and Sludge, "Determination of Ammonium-Nitrogen by Flow Analysis (E23)," DIN Method Number 38 406, December 1991.

2. Reardon, J.; Forman, J. A.; Seary, R. L. *Clin. Chim. Acta* **1966**, *14*, 403.

3. Methods for Chemical Analysis of Water and Wastes, March 1984, EPA-600/4-79-020, "Nitrogen Ammonia" Method 350.1 (Colorimetric, Automated Phenate).

4. Methods for Chemical Analysis of Water and Wastes, March 1984, EPA/4-79-020, "Nitrogen, Kjeldahl, Total" Method 350.2.

Ammonia Nitrogen DIN Table, SFA

RANGE,		0.1-1.0mg/L	1-10mg/L	
PUMP				
Speed	Percent	50	50	
Tubes	Buffer(R1)	blk/blk	blk/blk	
	Nitrogen	orn/yel	orn/yel	
	Salicylate(R2)	blk/blk	blk/blk	
	DIC(R3)	blk/blk	blk/blk	
	Debubble	blk/blk	blk/blk	
	Pull-off	orn/orn	orn/orn	
	Sampler Wash	grn/grn	grn/grn	
	Sample	blk/blk*	blk/blk*	
DETECTOR				
510	Wavelength	640nm	640nm	
	Rise time	10 sec.	1 sec.	
	Range	0.1 AUFS	1.0 AUFS	
505	Wavelength	640nm	640nm	
	Damp time	10 sec.	1 sec.	
	Range	0.1 AUFS	1.0 AUFS	
SAMPLER				
	Rate	48/hr	48/hr	
	Sample time	30 sec.	30 sec.	
	Wash time	45 sec.	45 sec.	
	Pecking	On	On	
	Start-up soln.	Brij-water	Brij-water	
	Wash soln.	Deionized Water	Deionized Water	
COMPUTER				
	Input voltage	0 to +1V	0 to +1V	
	(for 510)			
	Input voltage	0 to +1V	0 to +1V	
	(for 505)			
VALVE				
	Injection loop	N/A	N/A	

*You may wish to use a Helper line for this application. See the product insert titled "Helper Line Instructions" included in the accessory kit with your sampler.

Parameters were established to be a guideline and slight variations may be necessary to obtain optimal results.

Detector and computer settings are based on the opaque tan flowcell. If you have a different flowcell, these recommendations will have to be adjusted. Change either the computer setting or the detector range to compensate for the difference in sensitivity.

Ammonium-Nitrogen (DIN 38406) Flow Diagram SFA