



Overview Ammonia in wastewater is determined by method of known addition using an automated system of the Orion 960 Titrator and the Autotration-500 autosampler with an Orion 9512HP ammonia electrode. This procedure adds aliquots of 100mg/L NH₄Cl standard to the prepared sample and is adapted from EPA-Approved Standard Methods 4500-NH₃ E.

Market Environmental

Species Measured Ammonia

Sample Wastewater

Sample Size 50mL

Typical Concentration 0.6 mg/L

Technique # 2 Multiple Known Addition

Electrode Ammonia 9512HPBNWP

Solutions 0.1mg/L NH₄Cl as N std; 1.0mg/L NH₄Cl as N std; 100mg/L (0.00714M) NH₄Cl as N std. (951207); pH ISA Adjustor (951011); Internal Fill Solution (951209); Deionized Water; Rinse Solution (pH 4 buffer with 0.1M KCl)

Solutions preparation: 1.0mg/L std: 10mL of 100mg/L std to 1L with DI water. 0.1mg/L: 1mL of 100mg/L to 1L with DI water. Rinse Solution: dissolve 3.72g KCl in 500mL pH 4 buffer.

Titrant standardization: Not applicable

Sample Prep Pipet 50mL of each sample into a 150mL beaker. Place beakers in autosampler tray. Use the Autotration-500 autosampler unit (AT5150) for this analysis. 0.5mL of ISA will be added to each sample immediately before analysis by an auxiliary dispenser (096010).

If not analyzing sample immediately (w/in 15 minutes) following collection, the sample must be acidified with H₂SO₄ to pH<2 and stored at <6degC in a plastic, teflon or glass container for up to 28 days. Per Standard Methods 4500-NH₃ D.1.b., sample distillation is unnecessary. Check with local regulators when testing for reporting purposes.

Statistics

of Trials 4 **Mean** 0.67mg/L **%CV** 2.2 **Analysis Time** 5.6 minutes

Comments Condition probe in 1mg/L std w/ISA prior to testing. Check slope using low level slope check in manual. Check drift by comparing 2 & 3 min readings in 1mg/L std w/ISA (should be < 0.5mV). Measure at least one 1mg/L std and blank by known addition daily.

Use the autosampler rack which holds 28 beakers (ATR150). Set up 4 rinse beakers with the prepared rinse solution. Rinse time should be 30 seconds per beaker for best results. Use electrode holder CAS0050000 with the stirrer placed in the angled position.

Method Parameters

Sample Volume/Weight 50.0mL

Timed or Stability Readings 0.5mV/minute stability

Constant Increment 10.0mV

Number of Endpoints n/a

Max Titrant Volume 5.00mL

Desired Units mg/L

Molecular weight 14.00g

Predose 0.052mL

Prestir 1.0 second(s)

Additional Parameters A second dispenser must be used to add 0.5mL of pH adjusting ISA to each sample directly before measurement is made. Total Solution Volume is 50.5mL. Precision should be set to 2.0%.

Reaction Ratio 1.00



Results

METHOD 5 SUMMARY

SAMPLE ID NUMBER: 19
 TEST: _____
 SITE: _____
 ANALYST: _____
 11:45 06-20-08 ELECTRODE: 1:NH3
 TECHNIQUE 2 MULTIPLE KNOWN ADDN
 TOTAL SOLN VOL 50.500 mL
 SAMPLE VOLUME 50.000 mL
 STANDARD .007140 M of NH4Cl _____
 DISPENSER 1
 STIRRER 1
 PRE-DOSE VOLUME 0.052 mL
 PRECISION 2.0 %
 CONST INCREMENT 10.0 mV
 AUXILIARY REAGENT VOL 0.500 mL
 DISPENSER 2
 MAX STANDARD VOL 5.000 mL
 STABILITY CRITERION 0.5 mV/min
 PRESTIR 1.0 sec
 CONTINUOUS STIRRING
 REACTION RATIO 1.0000
 MOLECULAR WEIGHT 14.00
 CAL CONSTANT(1) 1.01717
 CAL CONSTANT(2) 1.05914

0 v= 0.051 mL E= 109.8 mV 47 sec
 -0.0 mV/min drift +/- 0.0 mV noise
 1 v= 0.356 mL E= 95.2 mV 44 sec
 -0.4 mV/min drift +/- 0.0 mV noise
 2 v= 0.966 mL E= 79.7 mV 34 sec
 -0.1 mV/min drift +/- 0.0 mV noise
 S= -56.9 Eo=-133.7 unkn= .650
 3 v= 2.950 mL E= 57.4 mV 38 sec
 -0.3 mV/min drift +/- 0.0 mV noise
 S= -57.8 Eo=-136.9 unkn= .669
 std dev= 0.0 mV precn= 1.4 %

3.3 min

MULTIPLE INCREMENT ANALYSIS

SAMPLE = .669 mg/L +/- 1.4%

SPIKE RECOVERY= 100.3%

RECOVERY ERROR= 0.3%

Note: It is recommended to re-run a sample if any of the following occur during the analysis as these indicate poor electrode performance.

- Calculated slopes (S) are less than 50
- Slow response (greater than 10 minutes for complete analysis) at concentrations greater than 0.05mg/L
- Error message: “wrong technique selected: switching to technique 3”
- Error message: “std dev out of range”
- Calculated precision (precn) greater than 10% (not applicable for blanks)
- Spike Recovery not within 100 +/- 2% for samples greater than 0.05mg/L
- Recovery Error greater than 2% for samples greater than 0.05mg/L

Be sure that the stirrer is in the angled position of the holder and located directly below the electrode surface. If the results are still poor, check the electrode in a standard and refer to electrode manual if standard has poor recovery. If standard has good recovery there may be an interference present in the sample; check manual for possible interferences.

Spike in Wastewater Matrix

	mg/L	% Recovery
Wastewater	0.67	
Spike	1.00	
MS	1.68	101%
MSD	1.67	100%