



**Overview** Ammonia in wastewater is determined using the method of known addition. This procedure is adapted from EPA-Approved Standard Methods 4500-NH3 E. Aliquots of 10mg/L standard are added to the prepared sample and measured using an Orion 9512HP ammonia electrode. The Orion 960 Titrator calculates electrode slope, sample concentration, and verifies the results via spike recovery.

**Market** Environmental

**Species Measured** Ammonia

**Sample** Wastewater

**Sample Size** 50mL

**Typical Concentration** 0.1mg/L

**Technique #** 2 Multiple Known Addition

**Electrode** Ammonia 9512HPBNWP

**Solutions** 0.1mg/L NH4Cl as N std; 1.0mg/L NH4Cl as N std; 10mg/L (0.000714M) NH4Cl as N std; 1000mg/L NH4Cl as N std (951007); pH ISA Adjustor (951211); Internal Fill Solution (951209); Deionized Water; Conditioning Solution (pH 4 buffer with 0.1M KCl)

**Solutions preparation:** 10mg/L std: 10mL of 1000mg/L std to 1L with DI water. 1.0mg/L std: 0.5mL of 100mg/L std to 500mL with DI water. 0.1mg/L std: 5mL of 10mg/L std to 500mL with DI water

**Titrant standardization:** Not applicable

**Sample Prep** Pipet 50mL of sample into 150mL beaker. 0.5mL ISA is added to sample immediately before analysis by an auxiliary dispenser or manually.

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** 6      **Mean** 0.108 mg/L      **%CV** 3.2      **Analysis Time** 4.8 minutes

**Comments** Conditioning Solution: dissolve 3.72g KCl in 500mL pH 4 buffer. Place probe in 50mL of this solution between measurements, stir 1 to 2 minutes then immerse in 2 beakers of DI water in sequence. Prior to testing, condition probe 15 min in 1mg/L std (w/ISA)

Check electrode slope daily according to low level slope check in manual. Check drift by comparing 2 & 3 min readings in 1mg/L std w/ISA (should be less than 0.5mV). Measure at least one 0.1mg/L std and a blank by known addition daily to check system.

## Method Parameters

**Sample Volume/Weight** 50 mL

**Timed or Stability Readings** 0.5 mV/minute stability

**Constant Increment** 5.0mV

**Number of Endpoints** n/a

**Max Titrant Volume** 5.0 mL

**Desired Units** mg/L

**Molecular weight** 14.00g

**Predose** 0.052mL

**Prestir** 1.0 second

**Additional Parameters** A second dispenser can be used to add 0.5 mL 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 4 SUMMARY

SAMPLE ID NUMBER: 2  
TEST: \_\_\_\_\_  
SITE: \_\_\_\_\_  
ANALYST: \_\_\_\_\_  
09:21 09-06-07 ELECTRODE: 1:NH3  
TECHNIQUE 2 MULTIPLE KNOWN ADDN  
TOTAL SOLN VOL 50.500 mL  
SAMPLE VOLUME 50.000 mL  
STANDARD .000714 M of \_\_\_\_\_  
DISPENSER 1  
STIRRER 1  
PRE-DOSE VOLUME 0.052 mL  
PRECISION 2.0 %  
CONST INCREMENT 5.0 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) 1.03264  
CAL CONSTANT(2) 1.00000

electrode check: +/- 1.7 mV

0 v= 0.052 mL E= 148.7 mV 131 sec  
0.0 mV/min drift +/- 0.0 mV noise  
1 v= 0.516 mL E= 133.7 mV 81 sec  
0.0 mV/min drift +/- 0.0 mV noise  
2 v= 2.169 mL E= 110.3 mV 85 sec  
-0.0 mV/min drift +/- 0.0 mV noise  
S= -58.0 Eo=-147.5 unkn= .102  
3 v= 3.769 mL E= 99.3 mV 55 sec  
-0.0 mV/min drift +/- 0.0 mV noise  
S= -57.8 Eo=-146.5 unkn= .101  
std dev= 0.0 mV precn= 0.7 %

5.4 min

MULTIPLE INCREMENT ANALYSIS

SAMPLE = .101 mg/L +/- 0.7%

SPIKE RECOVERY= 99.9%

RECOVERY ERROR= 0.1%

**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

Often times these errors are caused by a bubble on the membrane surface. Tap the electrode to remove bubbles and repeat test on fresh sample. 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.