

METHOD 1A

DETERMINATION OF AMMONIA IN EFFLUENTS COLLECTED IN ACID MEDIA USING THE SPECIFIC ION ELECTRODE

REF: Reg. 7-303

1. PRINCIPLE

- 1.1 This method is applicable to the determination of ammonia in effluents absorbed in dilute acid solution.
- 1.2 An aliquot of the acid absorbing solution is made alkaline with the addition of an ammonia pH adjusting solution (ISA), thus releasing the ammonia for determination by the specific ion electrode method.
- 1.3 This method is intended to measure the ammonia concentration in the range of 0.1 to 10 μg ammonia, as N, per 49 ml of sample aliquot. For solutions containing ammonia, as N, more than 10 μg per 49 ml, use less aliquot to bring the ammonia concentration to the working range of the standard curve.
- 1.4 Interference
 - 1.4.1 Sample color and turbidity do not interfere with the analysis.
 - 1.4.2 Volatile amines up to a concentration of 10% does not interfere.
 - 1.4.3 Mercury, which forms a very strong ammonia complex, does interfere. Treat samples containing mercury with sodium iodide to form a complex with mercury before measurement.
 - 1.4.4 Other metal ions such as copper, nickel, zinc, cadmium, may form complexes with ammonia. The presence of EDTA in the pH adjusting solution (ISA) forms complexes with these metals releasing the ammonia for analysis.

2. APPARATUS

- 2.1 Orion Model 920-A pH/Concentration/ISE Meter. Orion Research Inc. 529 Main Street, Boston, MA 02129 or equivalent.
- 2.2 Orion Ammonia Electrode, Model 95-12 or equivalent.
- 2.3 Magnetic Stirrer, Thermolyne S7805 or equivalent.
- 2.4 Magnetic Stirring Bars, 1 inch Teflon coated.

- 2.5 Graduated Cylinder, 50 ml capacity.
- 2.6 Beakers, Polypropylene, Tripour, 100 ml capacity.
- 2.7 Volumetric Pipets, Various sizes as needed.
- 2.8 Volumetric Flask, 500 ml capacity.
- 2.9 Membranes/cap for probe (Orion No. 951204 - box of 20 membranes or Cat. No. 951205 - bonded membrane caps - 3 per pack).

3. REAGENTS

- 3.1 Ammonia pH Adjusting ISA (Ionic Strength Adjuster). Orison Cat. # 951211.
- 3.2 Ammonia as Nitrogen Standard, 100 PPM. Orison Cat. # 951207
- 3.3 Ammonia as Nitrogen Standard, 1000 PPM. Orison Cat. # 951007
- 3.4 Ammonia Electrode Filling Solution. Orion Cat. # 951202
- 3.5 Hydrochloric Acid (0.01 N). To a 1 li volumetric flask containing approximately 800 ml of distilled water, pipet 0.84 ml of concentrated hydrochloric acid (37-38% assay) and dilute to the mark with distilled water. Cap the flask and invert it several times to mix the solution thoroughly.

4. ANALYTICAL PROCEDURE

- 4.1 After recording all the samples in the log book, check the pH of the solutions. Be sure that they are acidic. If the samples are alkaline, make them acidic with 0.1 N HCl (3.5) solution and then store them in the refrigerator.
- 4.2 All samples must be analyzed within five days of their submission to the laboratory.
- 4.3 Measure and record the total liquid volume of each impinger sample.
- 4.4 Set up the ion selective electrode and meter according to the manufacturer's instructions.
- 4.5 Calibrate the ion meter as described in Section 6. All calibration standards and samples must be at the same room temperature before making measurements.

- 4.6 Transfer up to a 49.0 ml aliquot of sample to a 100 ml polyethylene beaker containing a Teflon coated stirring bar.
- 4.7 Add 1.0 ml of ammonia pH adjusting ISA (if the sample does not turn blue upon addition, add ISA in 0.5 ml increments until blue color persists). (NOTES 1 & 2)
NOTE 1: Blue color persists when the solution is alkaline.
NOTE 2: Record the volume of the additional ISA that has been added and correct the dilution factor (DF) accordingly.
- 4.8 Immerse the precalibrated ammonia electrode into the sample and set the stirrer at low setting.
- 4.9 Record the concentration directly from the meter display when the ready prompt appears.
 - 4.9.1 Discard the sample if the meter reading is higher than 10 μg N/ml.
 - 4.9.1.1 Re-analyze the sample by repeating Sections 4.6 through Section 4.9 using less aliquot. Make up the volume of the solution to 49 ml with 0.01 N HCl. Record the dilution factor (DF).
 - 4.9.2 Discard the sample if the meter reading is less than 1 μg N/ml.
 - 4.9.2.1 Reanalyze the sample by repeating Section 4.6 through Section 4.9. Use 48 ml of sample then spike it with 0.5 ml (1 μg N/ml) of the 100 ppm standard. Make up the volume of the solution to 49 with 0.01 N HCl.
- 4.10 Recalibrate the ion meter with the 1.0 and 10.0 ppm ammonia as N standard after every fifth sample. Recalibrating the ion meter after every fifth sample has been found to be adequate.

5. STANDARD PREPARATION

- 5.1 Working Ammonia, as N, Standard Solution. Using a pipette transfer 50 ml of the 1000 ppm ammonia, as N, standard solution into a 500 ml volumetric flask and dilute to the mark with 0.01 N HCl. This working standard solution contains 100 μg ammonia, as N, per ml.
- 5.2 Prepare new working standards monthly.

6. CALIBRATION OF THE SPECIFIC ION ELECTRODE METER

- 6.1 Prepare two ion meter calibration solutions containing 1 ppm and 10 ppm ammonium nitrogen as follows: (NOTE 3)

NOTE 3: Calibration standards must be prepared prior to use.

6.1.1 Using a pipette, transfer 0.5 ml of the 100 ppm working standard into a 100 ml polypropylene beaker. Add 48.5 ml of 0.01 N HCl and 1.0 ml of ammonia pH adjusting ISA. Calibrate the meter according to the instrument manual with this 1 ppm ammonia, as N, standard.

6.1.2 Using a pipette, transfer 5.0 ml of the 100 ppm working standard into a 100 ml polypropylene beaker. Add 44 ml of 0.01 N HCl and 1.0 ml of ammonia pH adjusting, ISA, solution. Calibrate the meter according to the instrument manual with the 10 ppm N standard.

7. CALCULATIONS

$$7.1 \quad \mu\text{g Ammonia/ml} = \frac{\text{Meter reading}^* \times 60.71 \times \text{DF}}{\text{Aliquot (ml)}}$$

Where $60.71 = 50 \text{ ml} \times \frac{\text{M.W. ammonia}}{\text{M.W. nitrogen}}$

DF = Dilution Factor. If no dilution is made, then, DF = 1.

* When the sample is spiked with 1 ppm of N, subtract the 1 ppm spike from the meter reading prior to calculation.

8. REFERENCE

- 8.1 Benchtop pH/ISE Meter Instruction Manual, Orion Research Incorporated 1992
- 8.2 Model 95-12 Ammonia Electrode Instruction Manual, Orion Research Incorporated 1990
- 8.3 Purdue, H.L.; McNulty, P. J. Anal. Chem. 1988, 60, 1351 - 1354.
- 8.4 EPA Test Method 206 (Draft 1/10/96) - Procedure for Collection and Analysis of Ammonia in Stationary Sources.