Method no.:	ID-164
Matrix:	Air
OSHA Standard:	50 ppm
Collection procedure:	A known volume of air is drawn through a glass midget bubbler containing approximately 10 mL of 0.1 N H_2SO_4.
Recommended air volume:	120 liters
Recommended sampling rate:	1 liter per minute
Analytical procedure:	The volume of the bubbler solution is measured and diluted to volume, then analyzed by Ion Specific Electrode.
Detection limit:	2.0 µg NH_3 in solution
Precision and Accuracy:	(CV_T)=0.129
Method classification:	Partially Validated
Date revised:	December, 1988

1. Introduction

This method describes the collection and analysis of airborne ammonia.

1.1 History

Previously ammonia was analyzed using a calorimetric method and the Nessler reagent. This method had interferences and was subject to error due to old or contaminated Nessler reagent.

1.2 Uses (8.4)

The major uses of ammonia are in the manufacturing of fertilizer and explosives. Ammonia is also used in the petroleum, metallurgy, electronics, rubber, dye, photography, and aeronautics industries. It is most widely known in the form of household ammonia which is a dilute aqueous solution of ammonia.

1.3 Physical Properties (8.4)

Ammonia is a colorless gas at standard temperature and pressure. Commercial grades are approximately 99.5% pure. It is soluble in water, alcohol, ether, and organic solvents. Ammonia is caustic.

Physical Constants:

Density:	0.7710 g/L
Melting Point:	-77.7 °C
Boiling Point:	-33.350 °C
Molecular Weight:	17.03

2. Working Range and Detection Limit

2.1 The working range for ammonia analysis using this method is 2 µg to 850 mg NH_3. (8.2)

2.2 The detection limit obtained with the given conditions is approximately 2 µg.

3. Precision and Accuracy

3.1 The coefficient of variation (CV_T)= 0.129. This value was calculated from tabulated Quality Control samples in the range of 43 to 103 µg of NH_4 + (N=57). (8.5)

3.2 Factors which influence precision include electrode temperature, drift and noise. (8.1)

4. Interferences

4.1 The only species which interfere with this determination are volatile amines and metals which form strong complexes with ammonia. When hydroxide is present at the 0.1 N level and the ammonia concentration is below 10^{-3} M only mercury will appreciably complex ammonia. (8.2)

4.2 Volatile amines which interfere with the Nessler method also interfere with this electrode method. Preliminary studies show that levels which might occur in personal samples do not appreciably interfere. (8.3)

5. Advantages and Disadvantages

5.1 This method is a quick, simple, and selective way to analyze for ammonia concentration and it has a relatively large concentration range.

5.2 Anions, cations, and dissolved species do not interfere when standard and sample ionic strengths are

matched.

5.3 The sampling procedure uses bubblers containing 0.1 N H_2SO_4 which can be accidentally spilled causing slight acid burn discomfort.

6. Sampling Procedure Summary

6.1 10 mL of 0.1 N H_2SO_4 is placed in a glass midget bubbler.

6.2 The bubbler is attached to a personal sampling pump that has been calibrated in line with a representative loaded bubbler to an accuracy of ±10% at the 95% confidence level at the recommended flow rate (1 liter per minute).

6.3 The sampling pump with the bubbler attached is placed in the worker's breathing zone and about 120 liters of air is drawn through the bubbler. A minimum of 60 liters is recommended.

6.4 After sampling, the samples are shipped to the Laboratory in 20-mL scintillation vials. Vinyl or waterproof tape is wrapped around each cap to prevent leakage. Each cap is sealed with an OSHA Form 21. Each cap must have an inert polytetrafluoroethylene liner.

6.5 With each batch of up to 20 samples, the appropriate blank collection solution is submitted for analysis.

6.6. When ammonia compounds are known to be present in the workplace atmosphere, their identities should be listed.

7. Analytical Procedure

7.1 Apparatus

7.1.1 Ammonia Ion Specific Electrode - Orion model 95-10, 95-12 or equivalent. Between measurements, keep the electrode tip immersed in a 10 ppm standard with added NaOH. For storage overnight or longer, the electrode tip should be immersed in an 850 ppm standard without added NaOH.

7.1.2 Battery operated stirring rod.

7.1.3 Potentiometer - Orion 940 ionanalyzer or Altex 5000 SelectIon microprocessor-controlled instruments.

7.1.4 Calibrated personal sampling pump.

7.1.5 Midget impinger with absorbing solution of 0.1 N H_2SO_4.

7.1.6 Digital diluter capable of 1 mL uptake and 10 mL dispensing.

7.1.7 Associated laboratory glassware including volumetric flasks, polyethylene beakers, pipettes etc.

7.2 Reagents - All reagents used should be ACS analyzed reagent grade of better.

7.2.1 10 N NaOH prepared by dissolving 400 g NaOH in approximately 600-mL deionized water and diluting to one liter. Store in a polyethylene bottle.

7.2.2 Ammonia Stock Standard (1000 µg/mL NH3). Dissolve 3.141 g of NH_4Cl in absorbing solution (0.1 N H_2SO_4) and dilute to one liter. Store in a polyethylene bottle. Ammonia working standards are made by dilution of the stock standard solution.

7.2.3 Absorbing solution prepared by diluting 5.6 mL concentrated H2SO4 to 2 liters with deionized water.

7.2.4 Electrode filling solution containing ammonium chloride Orion Cat. No. 95-10-02 (for model 95-10) or 95-12-02 (for model 95-12).

7.3. Safety Precautions

7.3.1 Care should be exercised when using laboratory glassware. Chipped pipettes, volumetric flasks, beakers, or any glassware with sharp edges exposed should not be used to avoid the possibility of cuts, abrasions, and lost samples.

7.3.2 Pipetting should never be done by mouth. A bulb should always be used.

7.3.3 Be careful not to spill the absorbing solution onto the skin while making transfers, dilutions etc. as it will cause minor acid burns.

7.4. Standard Preparation

7.4.1 Rinse all previously cleaned glassware and plastic ware with 0.1 N H_2SO_4 and deionized water prior to use.

7.4.2 1000 ppm stock standard NH_3 solution listed in 7.2.2 is prepared. Dilutions of this stock are made using 0.1 N H_2SO_4 and are stored in polyethylene bottles. Standards below 100 ppm NH_3 should be prepared daily.

7.4.3 Working standards are prepared in the analytical range of 0.5 µg/mL to 100 µg/mL NH_3 from dilutions of the 1000 µg/mL stock solution. These standard solutions should be prepared fresh daily.

7.4.4 The dilution scheme is as follows:

Standard used	Dilution	Final Concentration
1000 ppm NH_3	20mL:200mL	100 ppm NH_3
100 ppm	50mL:500mL	10 ppm
100 ppm	25mL:500mL	5 ppm
5 ppm	50mL:500mL	0.5 ppm

7.5. Sample Preparation

7.5.1 Measure the sample volume in a graduated cylinder and record it.

7.5.2 Calibrate the digital diluter to withdraw 0.5 mL of sample and 9.5 mL of absorbing solution.

7.5.3 Dispense sample and absorbing solution into a 100-mL polyethylene beaker. Note: a larger sample aliquot might be needed if the air volume drawn is low.

7.5.4 Add 40 mL of 0.1 N H_2SO_4 to the beaker to make the final volume 50 mL.

7.6 Analysis

7.6.1 The following is a general synopsis of the analytical procedure. After the sample volume has been measured and an aliquot quantitatively diluted to a known volume, the sample pH is made alkaline using NaOH in order to convert virtually all ammonium to ammonia. The sample concentration of ammonia is determined by a standard addition technique using the ammonia gas-sensing Ion Specific Electrode.

7.6.2 The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from the electrode internal solution of ammonium chloride. Dissolved ammonia in the sample solution diffuses through the membrane until the partial pressure of ammonia is the same on both sides of the membrane. In any given sample, the partial pressure of ammonia will be proportional to its concentration. (8.2)

7.6.3 The ammonia-ammonium ion equilibrium in the filling solution determines the hydrogen ion concentration which is monitored by changes in potential of the glass pH electrode relative to a silver-silver chloride reference electrode. Both of these electrodes dip into the filling solution of the ammonia Ion Specific Electrode.

7.6.4 The ammonia electrode is assembled according to the instruction manual. Note: use either of the two electrodes. Model 95-12 uses a rectangular membrane which is placed across the end and held in place by the threaded cap. For model 95-10 the bottom cap assembly contains two o-rings, one red and one black. The black one is smaller than the red and fits into a groove of the spacer. The spacer with the black o-ring facing down should be placed on top of the membrane after positioning.

7.6.5 Fill the outer body of the electrode about 2/3 full with the appropriate internal filling solution.

7.6.6 The potentiometer to be used should be zeroed according to the instruction manual for that instrument. Instructions for the Orion 940 are listed in Table 1.

7.6.7 Use the slanted electrode holder which allows any gas bubbles to escape from the electrode membrane. If any bubbles are noticed on the membrane during the actual analysis, dislodge them by vigorously moving the electrode within the solution. If this is not done, erratic readings can result.

7.6.8 The working standards should be analyzed first to ensure the electrode is properly prepared for analysis. Pipette about 50 mL of 10, 5, and 0.5 ppm standard into separate 100-mL polyethylene beakers. These standards should be repeated periodically throughout the analysis. Other standards in this range can also be used if desired.

7.6.9 Add 1 mL 10 N NaOH to the solution being analyzed but do not do this until the electrode has been immersed in the solution and the stirring rod is operating.

7.6.10 Place the electrodes into the solution to approximately the same depth each time, making sure the stirring rod does not contact the electrode and is stirring at a moderate rate, i.e. no vortex present.

7.6.11 Follow the instruction manual for the instrument being used as to the proper way to do a standard addition analysis. (See Table 1 for instructions for the Orion 940) For either instrument the electrode is immersed in the solution and allowed to stabilize. For the Altex a set button is pushed which records this initial potential. The solution is spiked by adding 0.5 mL 1000 ppm NH_3. The instrument uses its microprocessor to determine solution concentration from the initial and final potentials and the concentration of the spike added. Note: There are no typical readings for the standards since this depends upon the membrane characteristics of the electrode.

7.6.12 Within the operating range of the electrode, reproducibility is independent of concentration. With calibration every hour, electrode measurements to ±2% can be obtained. The electrode exhibits good time response with 95% of total mV reading stabilization occurring in one minute or less for ammonia concentrations above 1 ppm. (8.2.)

7.6.13 The samples are analyzed by repeating steps 7.6.9 through 7.6.11. If the initial mV reading of a sample is greater than the initial mV reading of the high standard, then the sample must be diluted before it can be spiked and a final reading taken. This dilution is done with 0.1 N H_2SO_4.

7.7 Calculations

7.7.1 A least squares plot of final instrument reading versus ppm concentration of standards is made using the colorimetric program. This curve is used to calculate the concentration of NH_3 in ppm for each sample.

7.7.2 Air concentration values are calculated by the following equation:

$$\frac{\text{mg}}{\text{m}^3} = \frac{\text{(calculated ppm)(dilution factor)(sample volume, mL)(50mL)}}{\text{(aliquot volume, mL)(air volume sampled, L)}}$$

Air concentrations in ppm are obtained by using a conversion factor of 1.438.

$$\text{ppm} = \text{mg/m}^3 \times 1.438$$

8. References

8.1 Evans, W.H. and Partridge, B.F. *Analyst* 99, 367-375 (1974).

8.2 Instruction Manual, Ammonia Electrode Model 95-10, Orion Research Incorporated.

8.3 Baily, P.L., and Riley, M. *Analyst* 100 145-156 (1975).

8.4 *Merck Index*, Ninth Ed., 1976.

8.5 Tabulated data from OSHA Analytical Laboratory Quality Control Division.

Table 1.

Analysis using the Orion 940 follows a menu array. Answer the questions of the menu appropriately by using the "Yes," "No" and the numeric keys as follows:

OPERATOR MENU?	Answer "YES."
CHANGE ELECTRODE ID?	Answer "YES."
ELECTRODE 2 = F- IS THIS CORRECT?	Answer "NO" to change the ID. Continue to answer "NO" until NH_3 is displayed as a choice. Use the numeric keys to change the display to...
ELECTRODE 2 = NH3 IS THIS CORRECT?	Answer "YES."
SET ABSOLUTE OR RELATIVE MILLIVOLTS?	Answer "NO."
CHANGE THE pH OR ISE LIMITS?	Answer "NO."
SET TIMER?	Answer "NO."
CHANGE PRINT INTERVAL?	Answer "NO."
SET TEMPERATURE?	Answer "NO."
CHANGE THE TIME AND DATE?	Answer "NO."
ENTER STANDBY MODE?	Answer "NO."
OPERATOR	Answer "NO."

Enter "Speed 0" to continue after checking the Operator Menu.

CALIBRATE BY DIRECT MEASUREMENT?	Answer "NO."
USE INCREMENTAL TECHNIQUES?	Answer "YES."
1 = KA 2 = KS 3 = AA 4 = AS	Enter 1 to select known addition.
1 = SINGLE INCREMENT 2 = DOUBLE INCREMENT	Enter 1 to select single increment.
2-NH_3 ELECTRODE IN SAMPLE?	Place electrode and stirrer into the 1 ppm standard and add 1 mL of 10 N NaOH
SAMPLE VOL = 100.00 IS THIS CORRECT?	Answer by changing the volume using the numeric keys and then answer "YES" when the correct sample volume is displayed.
SLOPE = -59.2 mV/DEC IS THIS CORRECT?	Use the numeric keys to correct the slope if necessary and answer "YES."
EMF = XXX.X mV NOT READY	Wait for the reading to stabilize, and the display to change to....
EMF = XXX.X mV YES TO CONTINUE	Electrode response has stabilized press "YES" to continue.
STD ADDED TO SAMPLE?	Add 1 mL of 1000 ppm NH_3 standard to the sample and answer "YES."

STD CONCN = 1.0000 IS THIS CORRECT?	Use the numeric keys to change the concentration to 1000.0. Answer "YES."
STD VOL = 10.000 IS THIS CORRECT?	Use the numeric keys to change the volume to 1 and answer "YES."
EMF = XXX.X NOT READY	Wait for the reading to stabilize.
EMF = XXX.X YES TO CONTINUE	Press "YES" to continue.
2-NH_3 CONCN = 1.00 REPEAT TECHNIQUE?	Record this concentration in your record book. Rinse the electrodes with deionized water and blot dry. Then press "YES" to continue. Follow this procedure until all samples and standards have been read. Enter "speed 8" to return to "ENTER STANDBY?" Answer "YES."