

## Ammonia in Workplace Atmospheres – Solid Sorbent



Method No.:	ID-188
Matrix:	Air
OSHA Permissible Exposure Limits*	35 ppm [Short-Term Exposure Limit (STEL)]
Final Rule Limit (ammonia):	20 mg/m <sup>3</sup> STEL*
Final Rule Limits (ammonium chloride fume):	10 mg/m <sup>3</sup> [Time Weighted Average (TWA)]*
(ammonium chloride fume or ammonium sulfamate):*	
Transitional Limit:	50 ppm TWA
Collection Device:	For ammonia collection, a personal sampling pump is used to draw a known volume of air through a glass tube containing carbon beads impregnated with sulfuric acid (CISA).
Recommended Sampling Rates	
TWA Determinations:	0.10 liter per minute (L/min)
STEL Determinations:	0.5 L/min
Recommended Air Volume	
TWA:	24 L
STEL:	7.5 L
Analytical Procedure:	The sample is desorbed with deionized water and analyzed as ammonium ion using an ion chromatograph.
Detection Limits Qualitative:	0.60 ppm (24-L air sample) 1.9 ppm (7.5-L air sample)
Quantitative:	1.5 ppm (24-L air sample) 4.8 ppm (7.5-L air sample)
Precision and Accuracy	
Validation Range:	30.7 to 101.8 ppm
CV <sub>T</sub> :	0.050
Bias:	-0.009
Overall Error:	±10.9%
Method Classification:	Validated Method

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\*Note: Ammonium chloride fume or ammonium sulfamate can be sampled and analyzed using this method. A mixed-cellulose ester filter, polystyrene cassette, and personal sampling pump (2 L/min) are used to collect the sample. Samples are analyzed by ion chromatography after resorption in deionized water.

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Commercial manufacturers and products mentioned in this method are for descriptive use only and do not constitute endorsements by USDOL-OSHA. Similar products from other sources can be substituted.

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## 1. Introduction

This method describes the sample collection and analysis of airborne ammonia. Ammonium chloride fume or ammonium sulfamate can also be analyzed using this method. Samples are taken in the breathing zone of workplace personnel and are analyzed by ion chromatography (IC).

### 1.1. History

#### 1.1.1. Sampling

The previous OSHA sampling procedure for ammonia involved the use of a midjet fritted glass bubbler containing 0.1 N sulfuric acid ( $\text{H}_2\text{SO}_4$ ) (8.1, 8.2). Bubbler sampling is inconvenient to use. It involves the use of a liquid which if spilled may be irritating to the skin or may damage sampling pumps. Also, the sample solutions may leak during shipment.

The present method employs glass tubes containing CISA which avoids liquid sampling media problems. It is based on a procedure described by Bishop, et. al. (8.3).

#### 1.1.2. Analysis

Two analytical procedures have previously been used by OSHA. In the earliest procedure, ammonia was analyzed by a colorimetric method using Nessler reagent (8.2, 8.4). This method has significant interferences. The most recent method involved the use of the ammonia ion specific electrode (ISE) which does not discriminate between ammonia and amines (8.1).

The present method provides an analytical procedure which is easily set up and automated. Partial processing of the data is performed while the analysis is in progress.

1.1.3. An alternate screening technique for measuring ammonia exposures in the workplace involves the use of detector tubes (8.5). Other methods are needed to determine long-term ammonia concentrations since short-term detector tubes offer only spot checks of the environment.

### 1.2. Principle

A known volume of air is drawn through a sampling tube containing carbon beads impregnated with sulfuric acid (CISA). Ammonia is collected and converted to ammonium sulfate. Samples are desorbed using a known volume of deionized water (DI  $\text{H}_2\text{O}$ ) and analyzed as ammonium ion by IC. For ammonium chloride fume or ammonium sulfamate, samples are collected on 0.8- $\mu\text{m}$  mixed-cellulose ester filters, desorbed in DI  $\text{H}_2\text{O}$ , and also analyzed as ammonium ion by IC.

### 1.3. Advantages and Disadvantages

1.3.1. This method has adequate sensitivity for determining compliance with the OSHA permissible exposure limit (PEL) for workplace exposures to ammonia.

1.3.2. The method is simple, rapid, and easily automated.

- 1.3.3. Previous IC methods for ammonia have described rapid loss of peak resolution resulting primarily from metal-column binding. Using equivalent equipment described in Section 6.2 eliminates eluent contact with metal surfaces, subsequent corrosion and rapid loss of resolution due to metals binding on the separator column.
- 1.3.4. Previous studies have also indicated changes in ammonium peak characteristics with changes in pH. When using the equipment and conditions described herein, retention times or peak shapes were not significantly affected when the diluent concentration was from 0.0001 to 0.02 N H<sub>2</sub>SO<sub>4</sub>. The peak characteristics were significantly different when a diluent of 0.1 N H<sub>2</sub>SO<sub>4</sub> was used. (Note: due to the H<sub>2</sub>SO<sub>4</sub> on the beads, a 25 mL solution volume = 0.02 N H<sub>2</sub>SO<sub>4</sub>).
- 1.3.5. Potential exposure to H<sub>2</sub>SO<sub>4</sub> is reduced in comparison to previous methods for ammonia.
- 1.3.6. The analysis is specific for the ammonium ion (NH<sub>4</sub><sup>+</sup>).
- 1.3.7. After sample preparation (and acidification with additional H<sub>2</sub>SO<sub>4</sub>), ammonia can also be determined by the ISE analytical technique (8.1) or a calorimetric procedure (8.2).
- 1.3.8. One disadvantage is that ammonium salts present in the air as dust would constitute a positive interference; however, particulate will be captured in the glass wool plug preceding the acid-treated beads. A polystyrene cassette containing a mixed-cellulose ester filter can also be used as a prefilter to collect any particulate.
- 1.3.9. Another disadvantage is the positive interference from monoethanolamine, isopropanolamine, or propanolamine. If present, these compounds will produce peaks in the vicinity of the ammonium ion when using this method. Mobile phase ion chromatography (8.6) can be used for confirmation of ammonia if these compounds are present.

#### 1.4. CAS No. and Physical Properties (8.7, 8.8)

##### Ammonia

CAS No.:	7664-41-7
Chemical formula:	NH <sub>3</sub>
Formula weight:	17.03
Boiling point:	-33.35 °C
Melting point:	-77.7 °C
Density, gas (air = 1):	0.5967
Density, liquid:	0.6818 (-33.35 °C)
Critical temperature:	132.4 °C
Critical pressure:	11.3 × 10 <sup>3</sup> kPa
Autoignition temperature:	651 °C
Flammable limits:	16-25% (by volume in air)
Solubility	

Cold water (0 °C):	89.9 g/100 cc
Hot water (100 °C):	7.4 g/100 cc
Color:	Colorless
Lower limit of perception:	Approximately 20 ppm

Ammonium chloride CAS No.: 12125-02-9

Ammonium sulfamate CAS No.: 7773-06-0

Chemical formula

Ammonium chloride:  $\text{NH}_4\text{Cl}$

Ammonium sulfamate:  $\text{NH}_4\text{OSO}_2\text{NH}_2$

### 1.5. Prevalence and Use

Ammonia is a widely used chemical, being involved in the manufacture of fertilizers, nitric acid, explosives, and synthetic fibers. It is also used in refrigeration (8.8). Occupations with the potential for exposure to ammonia include the following (8.7):

Amine workers	Fertilizer workers
Ammonia workers	Glass cleaners
Ammonium salt makers	Maintenance workers (janitors)
Aniline makers	Manure handlers
Case hardeners	Nitric acid makers
Chemical laboratory workers	Organic chemical synthesizers
Chemical manufacturers	Petroleum refinery workers
Coal tar workers	Refrigeration workers
Color makers	Rocket fuel makers
Compressed gas workers	Sewer workers
Cyanide makers	Soda ash makers
Dye makers	Solvay process workers
Explosive makers	Tanners
Farmers	Urea makers

### 1.6. Toxicology (8.7, 8.9, 8.10)

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Note: Information contained within this section is a synopsis of present knowledge of the physiological effects of ammonia and is not intended to be used as a basis for OSHA policy.

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Ammonia forms a strong alkaline solution in water, and the high solubility and strong alkalinity make it especially irritating to the upper respiratory system. Exposure to ammonia can occur not only from the vapor but also from the liquid and from concentrated aqueous solutions. Depending upon the exposure, symptoms can range from mild upper respiratory irritation to inflammatory processes of the entire respiratory tract with complications of pulmonary edema and bronchopneumonia. Symptoms may also include hoarseness and tightness in the throat. The odor threshold for ammonia varies among the reports received; 50 ppm is known to produce a strong odor. Brief exposure to 100 ppm increases nasal air flow resistance, possibly from

vascular congestion, edema and increased mucus secretion. Mild irritation of the eyes, nose and throat is produced by 50 ppm but not by 25 ppm. Acclimation appears to develop to 50 ppm within one week, and to 100 ppm within 2 to 3 weeks of repeated exposure. Volunteers exposed to 500 ppm for 30 minutes experienced hyperventilation and an increase in respiratory rate. Exposure to 1,000 ppm produced immediate coughing. Exposures to 700 to 1,700 ppm can be incapacitating due to extreme lacrimation and coughing. The eyes, skin and respiratory tract may be severely inflamed. Massive accidental exposure can be quickly fatal; autopsies of individuals who have died from exposure have indicated severe damage at every level of the respiratory system, including edema and hemorrhage. Skin burns from exposure to liquid ammonia can also occur. Ammonia is irritating to the eyes; failure to irrigate the eyes with a considerable amount of water following heavy exposure may lead to blindness.

## 2. Range, Detection Limit and Sensitivity (8.11)

- 2.1. This method was validated over the concentration range of 30.7 to 101.8 ppm. Air volumes of about 21 L and flow rates of about 0.1 L/min were used. The average sampling time was 210 min.
- 2.2. The qualitative detection limit was 0.2 µg/mL or 10.0 µg (as NH<sub>3</sub>) when using a 50-mL solution volume. This corresponds to 0.60 ppm NH<sub>3</sub> for a 24-L air volume. The quantitative detection limit was 0.50 µg/mL or 25 µg (as NH<sub>3</sub>) when using a 50-mL solution volume. This corresponds to 1.5 ppm NH<sub>3</sub> for a 24-L air volume. A 50-µL sample loop and a 30 microsiemens detector setting were used for both IC detection limit determinations. 2.3 The sensitivity of the analytical method, when using the instrumentation specified in Section 6.2, was calculated from the slope of a linear working range curve (1 to 10 µg/mL ammonium ion). The sensitivity was 12,380 area counts per 1 µg/mL ammonium ion (a Dionex Autolon 400 data reduction system was used). Data manipulation was also performed using a Hewlett-Packard 3357 Laboratory Automation System. The sensitivity for this system was 361,000 area counts per 1 µg/mL ammonium ion (1 area count = 0.25 microvolt-second for the Hewlett-Packard system).

## 3. Method Performance (8.11)

Test results are based on samples collected from an in-house dynamic generation system at flow rates of approximately 0.1 L/min and sampling times of 180 to 240 min. Exceptions are noted below.

- 3.1. The pooled coefficient of variation (CV<sub>T</sub>) for samples taken in the range of 30.7 to 101.8 ppm was 0.050. The method exhibited slight negative bias (-0.009). Overall error was within acceptable limits at ±10.9%.
- 3.2. The collection efficiency at about 2 times the PEL was 100%.
- 3.3. Breakthrough tests were performed at a concentration of 258 ppm, 50% RH, and 25 °C. Breakthrough of ammonia into backup sections of sorbent was undetectable. Samples were collected for 335 min.
- 3.4. Samples can be stored at ambient (20 to 25 °C) laboratory conditions for at least 29 days. The mean recovery of samples analyzed after 29 days was within 5% of the mean recovery of samples analyzed after 1 day of storage. Samples were stored in an office desk.
- 3.5. Sampling tubes stored 11 months before use gave satisfactory results during validation experiments.

#### 4. Interferences

- 4.1. When other compounds are known or suspected to be present in the air, such information should be transmitted with the sample.
- 4.2. Any compound having the same retention time as the ammonium ion, is an interference. The following compounds were noted as potential interferences with ammonium ion when using the equipment and conditions stated in Section 6:

Methyl- and dimethylamine, mono- and diethanolamine, iso- and propanolamine.

- 4.2.1. Methylamine and ammonium are not separated well in a 1:1 mixture (Figure 1a and 1b). Dimethylamine and ammonium in a 1:1 mixture show better resolution (Figure 1c).

1. Both mixtures displayed diminished peak areas for the ammonium ion; however, ammonium peak heights were similar to the 10 µg/mL standard shown in Figure 1a. If an interference of this type is present, peak heights can be used for calculations instead of peak areas.

2. An alternate eluent (0.012 M HCl) offered sufficient resolution between ammonia and methyl- or dimethylamine (Figure 1d and 1e). This eluent can be used for confirmation if necessary.

- 4.2.2. A peak in the same vicinity as ammonia was noted when a dilute monoethanolamine (MEA) solution was analyzed (see Figure 1f). The detector response for MEA is about one-half that seen for ammonia at a concentration of approximately 10 µg/mL (Figure 1a and 1f). Separation of ammonium and MEA was not noted when a 1:1 mixture (10 µg/mL for each) was analyzed when using either the recommended or the alternate eluent.

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Note: The MEA used for this study contained trace contaminants as shown by peaks 1 and 3 in Figure 1f. These peaks probably represent trace amounts of sodium and potassium ions, respectively.

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- 4.2.3. Diethanolamine (DEA) also produces a response; however, this response is only noticeable at very large concentrations. A concentration of 10 µg/mL DEA did not produce a measurable peak.

- 4.2.4. Propanolamine and isopropanolamine elute at approximately the same time and with a similar response as MEA.
- 4.2.5 If necessary, the presence of ammonia, methyl- or dimethylamine, MEA, isopropanolamine or propanolamine can be confirmed using mobile phase ion chromatography (8.6).

- 4.3. Contaminant cations, such as Na<sup>+</sup> and K<sup>+</sup>, do not interfere when using the conditions and instrumentation specified. When using the conditions described in Section 6, peak retention times of individual 10 µg/mL solutions of various analytes were:

<u>Analyte</u>	<u>Retention Time (min)</u>
urea	no response
methanol	no response
diisopropanolamine	no response
triisopropanolamine	no response
diethanolamine (10 µg/mL)	no response
triethanolamine	no response
sodium	3.28
monoethanolamine	3.67
isopropanolamine	3.68
ammonium	3.70
propanolamine	3.77
diethanolamine (1,000 µg/mL)	3.80
methylamine	4.08
dimethylamine	4.17
ethylamine	4.35
diethylamine	4.77
potassium	4.83

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Note: The listing above is for information only. The majority of these analytes will most likely not be present when sampling for ammonia. Retention times may vary slightly.

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- 4.4. Interferences may be minimized by changing the eluent, eluent concentration or pump flow rate.
- 4.5. Complete separation and quantitation of low molecular weight alkyl amines as well as the alcoholic amines can be achieved using mobile phase ion chromatography (8.6) or alternate sampling and analytical methods (8.12, 8.13).
- 4.6. Alternate ISE or calorimetric methods can also be used (8.1, 8.2); however, interferences are a significant problem for both methods.
- 4.7. Ammonium salts present as dust would interfere; however, this material should be collected in the glass wool plug preceding the collecting medium. A prefilter consisting of a mixed-cellulose ester filter in a polystyrene cassette can also be used if a large amount of particulate is present in the atmosphere. Preliminary tests comparing sampling tubes with and without a prefilter did not indicate a significant difference in recoveries; therefore, ammonia did not react with the prefilter components. Tests were conducted using a dynamic test atmosphere of 184 ppm NH<sub>3</sub> at 50% RH and 25 °C.

## 5. Sampling

### 5.1. Equipment - Ammonia Sampling

- 5.1.1. Personal sampling pumps capable of sampling within ±5% of the recommended flow rate of 0.1 L/min.
- 5.1.2. Carbon bead, 20/30 mesh (Kureha Chemical Industry Co., 420 Lexington Ave., Suite 1742, NY, 10170, phone no. 212-867-7040).
- 5.1.3. Sampling tubes which contain an adsorbing section consisting of carbon beads treated with H<sub>2</sub>SO<sub>4</sub>. Tubes are commercially available, but may also be easily prepared

**(Caution:** Sulfuric acid can cause severe burns. Wear protective gloves, lab coat and eyewear when using H<sub>2</sub>SO<sub>4</sub>).

1. The commercially available tube consists of two sections; a 500-mg carbon bead front and a 250-mg backup section (ORBO-77 Tubes, cat. no. 582-12, Supelco Inc., Bellefonte, PA or SKC cat. no. 226-29, SKC, Eighty Four, PA).

2. Ammonia collection tubes may be prepared according to the method of Bishop, Belkin and Gaffney (8.3). The following is a variation of this method: Thirty-one sampling tubes can be prepared using 23 g of carbon beads. The beads are placed in a beaker, rinsed five times with 0.01 N H<sub>2</sub>SO<sub>4</sub> and then five times with DI H<sub>2</sub>O. Sufficient concentrated H<sub>2</sub>SO<sub>4</sub> (1.2 g of acid for 23 g of beads) is added so the final product, when dried, will consist of 5% acid by weight. Enough DI H<sub>2</sub>O to just cover the beads is also added and the contents are mixed. The product is dried at 110 °C overnight in a drying oven. The beads are mixed and then packed into glass tubes, 10 cm × 8 mm o.d. × 6 mm id. The front absorbing section contains 500 mg and the backup section 250 mg of carbon beads. Each section is held in place by glass wool plugs. The tubes are capped with plastic end caps or are fire sealed.

- 5.1.4. A stopwatch and bubble tube or meter are used to calibrate the pumps. A blank sampling tube or device is placed in-line during flow rate calibration.
- 5.1.5. Various lengths of flexible tubing are used to connect the sampling tubes to the pumps.
- 5.1.6. Mixed-cellulose ester filters and polystyrene cassettes can be used as prefilters if particulate are a potential problem. See Section 5.3 for further details.

## 5.2. Sampling Procedure - Ammonia

- 5.2.1. Calibrate the sampling pumps to the recommended flow rate of 0.1 L/min for TWA determinations or to 0.5 L/min for STEL measurements.
- 5.2.2. Connect the sampling tube to the pump such that air enters the larger (500 mg) section first.
- 5.2.3. Place the sampling tube in the breathing zone of the employee.
- 5.2.4. Sample with the pre-calibrated pump at the listed flow rate and sampling time. The recommended sampling time is 4-h for TWA assessments, giving a total air volume of about 24-L. For STEL determinations, sample for 15 min.
- 5.2.5. Prepare one sampling tube as a blank sample. Treat this tube the same as the samples except that no air is drawn through it.
- 5.2.6. Place plastic end caps on each tube after sampling. Attach an OSHA seal around each tube to secure the end caps. Send the samples along with a blank sample to the laboratory with the OSHA 91A paperwork requesting ammonia analysis.
- 5.2.7. Bulks can also be submitted for analysis. Ship bulk samples separately from air samples. They should be accompanied by Material Safety Data Sheets if available. Check current shipping restrictions and ship laboratory by the appropriate method.



### 5.3. Sampling for Ammonium Chloride or Ammonium Sulfamate

The following equipment is used:

1. Mixed-cellulose ester (MCE) filters (0.8 µm pore size), cellulose backup pads, and cassettes, 37-mm diameter (part no. MAWP 037 AO, Millipore Corp., Bedford, MA).
2. Gel bands (Omega Specialty Instrument Co., Chelmsford, MA) for sealing cassettes.
3. Calibrated sampling pumps - 0.1 to 2 L/min flow rate.

Connect the MCE filter/cassette assembly to a calibrated sampling pump and collect samples at a flow rate of about 2 L/min.

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Note: If the filters are to be used as prefilters, attach the cassette to the CISA sampling tube with a minimum amount of tubing, and attach the free end of the CISA tube to the sampling pump. Sample at a flow rate of 0.1 L/min if a prefilter is used.

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Sample for at least 15 min for STEL measurements and up to 8 h for TWA determinations. After sampling, seal and submit the samples to the laboratory. Request analysis for ammonium sulfamate or ammonium chloride.

## 6. Analysis

### 6.1. Precautions

- 6.1.1. Refer to instrument and standard operating procedure (SOP) manuals (8.14) for proper operation.
- 6.1.2. Observe laboratory safety regulations and practices. **Caution:** Sulfuric or hydrochloric acid can cause severe burns. Wear protective gloves, labcoat and eyewear when using these acids.

### 6.2. Equipment

- 6.2.1. Ion chromatography (Model 2010i, Dionex, Sunnyvale, CA) equipped with a conductivity detector.
- 6.2.2. Automatic sampler (Model AS-1, Dionex) and sample vials (0.5 mL).
- 6.2.3. Data processing system (Autolon 400 System, Dionex).
- 6.2.4. Printer.
- 6.2.5. Cation separator column (Model HPIC-CS3, Dionex).
- 6.2.6. Cation guard column (Model HPIC-CG3, Dionex).
- 6.2.7. Cation micromembrane suppressor (Model CMMS-1 suppressor, Dionex).
- 6.2.8. Disposable syringes (1 mL) and prefilters.

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(Note: Some prefilters are not cation- or anion-free. Tests should be done with blank solutions first to determine suitability for the analyte being determined).

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- 6.2.9. Polyethylene scintillation vials (20 mL) with polyethylene cap liners (Part No. 58515, Kimble, Toledo, OH).
- 6.2.10. Miscellaneous volumetric glassware: Beakers, graduated cylinders, beakers, and volumetric flasks (0.25 to 4 L).
- 6.2.11. Analytical balance (0.01 mg).
- 6.3. Reagents - All chemicals should be reagent grade or better
  - 6.3.1. Deionized water (DI H<sub>2</sub>O) with a specific conductance of less than 10 microsiemens.
  - 6.3.2. Hydrochloric acid (HCl) solution (1 N):  
Dilute 166 mL of concentrated HCl to 2.0 L with DI H<sub>2</sub>O.
  - 6.3.3. Strong eluent (48 mM HCl, 4 mM DAP-HCl, 4 mM L-histidine -HCl): Weigh 0.560 g 2,3-diaminopropionic acid monohydrochloride (DAP-HCl) and 0.840 g L-histidine monohydrochloride monohydrate and then place in a 1-L volumetric flask. Add 48 mL of 1 N HCl. Dilute to volume with DI H<sub>2</sub>O. Mix thoroughly. Prepare monthly.
  - 6.3.4. Weak eluent (12 mM HCl, 0.25 mM DAP-HCl, 0.25 mM L-histidine-HCl):

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Note: Prepare a new solution for each analysis. Aged solutions of weak eluent tend to lose buffering capacity. Chromatographic dips in the vicinity of the ammonium peak have been noted using aged eluent and may lead to erroneous results. These dips only occur with samples (which contain a small amount of sulfuric acid) and do not occur with standards (prepared with DI H<sub>2</sub>O).

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- Dilute 252 mL of strong eluent and 36 IRL of 1 N HCl to 4.0 L with DI H<sub>2</sub>O. Mix thoroughly.
- 6.3.5. Alternate eluent (12 mM HCl): This eluent is only used if potentially resolvable interferences are present (See Section 4.2.1 for further information). Dilute 48 mL of 1 N HCl to 4.0 L with DI H<sub>2</sub>O. Prepare a new solution for each analysis.
  - 6.3.6. Regeneration solution [0.04 N tetramethylammonium hydroxide (CH<sub>3</sub>)<sub>4</sub>NOH (TMAOH)] (Note: The purity of the reagent must be considered when preparing the 0.04 N TMAOH solution.): Commercially prepared solutions of 25% TMAOH can be used (25% TMAOH, cat. no. 33,163-5, Aldrich Chemical Co., Milwaukee, WI). Dilute 57.4 mL of 25% TMAOH to 4 L with DI H<sub>2</sub>O. An alternative preparation is to dissolve 29.00 g of tetramethylammonium hydroxide pentahydrate [(CH<sub>3</sub>)<sub>4</sub>NOH · 5H<sub>2</sub>O] in 4.0 L of DI H<sub>2</sub>O.
  - 6.3.7. The eluent used with CSRS suppressor, IonPac CS12 column, and CG12 guard column is 20 mM methane sulfonic acid (CH<sub>3</sub>SO<sub>3</sub>H) solution. Dilute 2.6 mL methane sulfonic

acid to 2.0 L with DI H<sub>2</sub>O (Methane sulfonic acid, cat. no. M860-6, Aldrich Chemical Co., Milwaukee, WI).

- 6.3.8. Sulfuric acid solution (0.1 N): Dilute 5.6 mL of concentrated H<sub>2</sub>SO<sub>4</sub> to 2.0 L with DI H<sub>2</sub>O.
- 6.3.9. Ammonia stock standard (1,000 µg/mL ammonia): Dissolve 3.141 g of ammonium chloride in 0.1 N H<sub>2</sub>SO<sub>4</sub> and dilute to the mark in a 1-L volumetric flask. Prepare every month.
- 6.3.10. Ammonia standard (100 µg/mL). Dilute 50 mL of the 1,000 µg/mL ammonia stock standard to 500 mL with DI H<sub>2</sub>O. Prepare weekly.
- 6.3.11. Ammonia standard (10 µg/mL). Dilute 50 mL of the 100 µg/mL ammonia stock standard to 500 mL with DI H<sub>2</sub>O. Prepare weekly.

#### 6.4. Working Standard Preparation

- 6.4.1. Ammonia working standards may be prepared weekly in the ranges specified:

Working STD (µg/mL)	Standard Solution (µg/mL)	Aliquot (mL)	Final Vol. (mL)
1	10	10	100
2	10	20	100
5	100	5	100
10	10	*	*
15	100	30	200
20	100	20	100

\* Already prepared in Section 6.3

- 6.4.2. Pipette appropriate aliquots from standard solutions prepared in Section 6.3 into volumetric flasks of the final volumes specified. Dilute to volume with DI H<sub>2</sub>O.
- 6.4.3. Pipette a 0.5- to 0.6-mL portion of each standard solution into separate automatic sampler vials. Place a 0.5-mL filter cap into each vial. The large exposed filter portion of the cap should face the standard solution. Also prepare a reagent blank from the DI H<sub>2</sub>O used for standard preparation.

#### 6.5. Sample Preparation - CISA Samples

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Note: For the CISA samples, always use a final solution volume >25 mL.

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- 6.5.1. Carefully remove and discard the glass wool plugs from the sample tubes, making sure that no sorbent is lost in the process. Transfer each sorbent section into individual polyethylene vials.
- 6.5.2. Add 10 mL of DI H<sub>2</sub>O to each vial, cover vials with polyethylene lined caps and then shake vigorously for about 30 s. Allow the solutions to settle for at least 1 h.

- 6.5.3. Quantitatively transfer each front section desorption solution to individual 25- or 50-mL volumetric flasks.
- 6.5.4. Rinse the beads in the vial with additional portions of DI H<sub>2</sub>O and also transfer this rinse to the flask. Take care so the beads are not transferred to the flask.
- 6.5.5. Dilute to volume with DI H<sub>2</sub>O. Also transfer each backup section resorption solution to individual 25- or 50-mL volumetric flasks and dilute to volume.
- 6.5.6. An alternate method of resorption and dilution is: Place the beads into 25- or 50-mL volumetric flasks. Measure the appropriate amount of DI H<sub>2</sub>O using a pipette or graduated cylinder and add this to the carbon beads.
- 6.5.7. If the sample solutions contain particulate, remove the particles using a prefilter and syringe. Fill the 0.5-mL automatic sampler vials with sample solutions and push a filtercap into each vial.
- 6.5.8. Load the automatic sampler with labeled samples, standards and blanks.
- 6.6. Sample Preparation - Ammonium Chloride Fume or Ammonium Sulfamate
  - 6.6.1. Open the filter cassette, carefully remove the sample filter with forceps, and place in a scintillation vial. If the cassette contains loose dust, carefully rinse the dust into the vial with DI H<sub>2</sub>O. If necessary, wipe out the dust with a clean MCE filter and place this filter in the vial. If the backup pad appears to be discolored, it may be due to leakage of air around the filter during sampling. In these cases, the pad should also be prepared and analyzed. Place the backup pad in a separate vial. Also prepare a blank backup pad.
  - 6.6.2. Add 10 mL of DI H<sub>2</sub>O to each scintillation vial. Allow to sit for at least 1 h with occasional agitation of the solution and filter. Proceed with the analysis as described in Sections 6.5.7-6.5.8 and 6.7
- 6.7. Analytical Procedure
  - 6.7.1. Set up the ion chromatography in accordance with the SOP (8.14) or instrument manuals.

Typical operating conditions for a Dionex 2010i with an automatic sampler are listed below:

Ion chromatograph

Eluent (Section 6.3.4):	DAP-histidine-HCl
Eluent conductivity:	approximately 7 microsiemens
Regenerant flow:	2 to 3 mL/min (0.04 N TMAOH)
Sample injection loop:	50 µL

Pump

Pump pressure:	approximately 550 psi
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Flow rate: 1 mL/min

Chromatogram

Run time: 5 min

Average peak retention time: 3.7 to 3.9 min

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Note: If the alternate eluent is used, allow a longer period of time for the ion chromatography to equilibrate (2 to 3 h). The retention time of the ammonium ion will be much longer with the alternate eluent.

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6.7.2. If an ion chromatography is not available, the sample solutions may be acidified with H<sub>2</sub>SO<sub>4</sub> to 0.1 N and analyzed with an ammonia ISE as described in Method No. ID-164 (8.1).

7. Calculations

7.1. After the analysis is completed, peak areas and heights can be retrieved using a variety of methods or programs (8.14). Hard copies of chromatograms, which list peak heights and areas, can be obtained from a printer. An example chromatogram containing 3 µg/mL sodium, 20 µg/mL ammonium, and 10 µg/mL potassium ions is shown in Figure 2.

7.2. Prepare a concentration-response curve by plotting the concentration of the standards in µg/mL (or µg/sample if the same solution volumes are used for samples and standards) versus peak areas or peak heights. Blank correct each sample section (sample and blank solution volumes should be the same). Add the backup section results to the front section results for each tube.

7.3. The concentration of ammonia in each air sample is expressed in ppm. The equation is:

$$\text{ppm NH}_3 = \frac{\text{molar volume} \times \text{ug/mL NH}_3 \times \text{solution volume (mL)}}{\text{formula weight} \times \text{air volume (L)}}$$

where:

molar volume = 24.46 (25 °C and 760 mm Hg)

formula weight (NH<sub>3</sub>) = 17.03

µg/mL NH<sub>3</sub> = Blank corrected value from Section 7.2

7.4. For ammonium chloride fume or ammonium sulfamate:

$$\text{mg/m}^3 \text{ analyte} = \frac{\text{ug/mL NH}_3 \times \text{solution volume (mL)} \times \text{GF}}{\text{air volume}}$$

where:

$\mu\text{g/mL NH}_3$  = Blank corrected value from Curve  
GF = Gravimetric Factor:  
Ammonium chloride ( $\text{NH}_4\text{Cl}$ ) = 3.14  
Ammonium sulfamate ( $\text{NH}_4\text{OSO}_2\text{NH}_2$ ) = 6.70

7.5. Report CISA results to the industrial hygienist as ppm ammonia. Report ammonium chloride or ammonium sulfamate results as  $\text{mg/m}^3$ . Ammonium chloride or sulfamate results are based on the analysis of the ammonium ion; other ammonium salts present in the air during sampling may be a positive interference.

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Interference Chromatograms

PEAK NUM	RET TIME	AREA	HEIGHT
1	3.18	2.445e+003	239
2	3.70	1.122e+003	6801

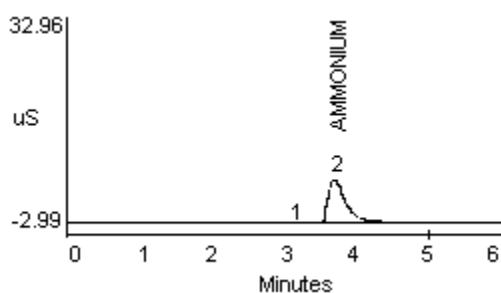


Figure 1a

PEAK NUM	RET TIME	AREA	HEIGHT
1	3.20	3.912e+003	345
2	3.73	7.910e+004	6081
3	4.00	1.936e+005	12221

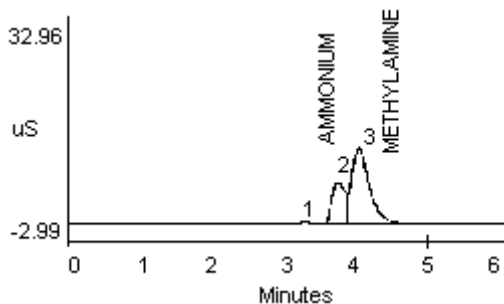


Figure 1b

PEAK NUM	RET TIME	AREA	HEIGHT
1	3.20	2.746e+003	276
2	3.72	9.505e+004	6867
3	4.08	1.558e+003	9673

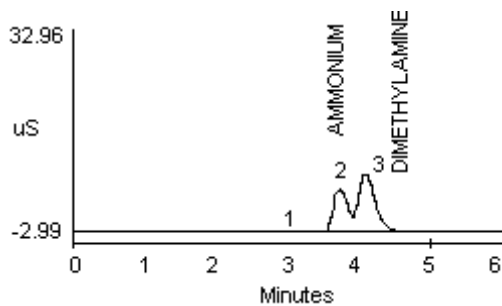


Figure 1c

PEAK NUM	RET TIME	AREA
1	13.52	1.366e+003
2	16.57	1.758e+005

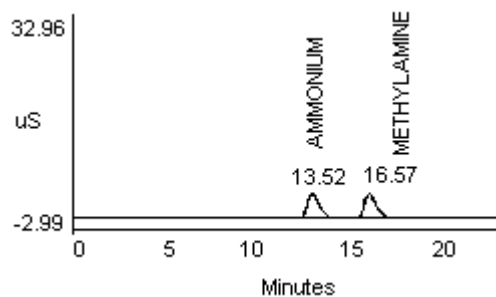


Figure 1d



PEAK NUM	RET TIME	CONC in ppm	AREA	height
1	13.45		1.477e+005	3838
2	19.23		1.475e+005	2854

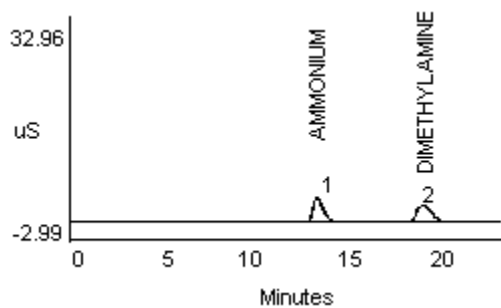


Figure 1e

PEAK NUM	RET TIME	AREA	height
1	3.18	2.260e+004	2021
2	3.67	4.183e+004	2949
3	4.72	8.419e+003	560

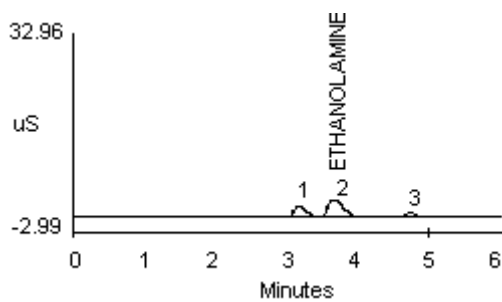


Figure 1f

Figure 1

All identified species are 10 µg/mL

Ion Chromatogram of Sodium, Ammonium, and Potassium Ions

PEAK NUM	RET TIME	AREA	HEIGHT
1	3.22	8.906e+004	7972
2	3.73	1.775e+005	10273
3	4.70	1.940e+005	11514

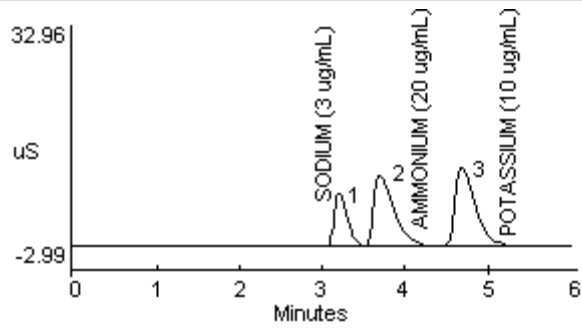


Figure 2

This backup report was revised June, 1990

## Introduction

The general procedure for the air sample collection and analysis of ammonia is described in OSHA Method No. ID-188 (10.1). The validation of this method examines the use of a glass sampling tube containing 500 mg of carbon bead impregnated with sulfuric acid (CISA). Sampling tubes were made in-house and also obtained from Supelco Inc. (Bellefonte, PA). During the validation these commercial tubes became available and were used for experiments not completed. The in-house and commercially prepared tubes are identical except the tube manufactured by Supelco has a 250-mg backup section. The in-house tubes were prepared using the method of Bishop, Belkin and Gaffney (10.2) with a minor modification. A dilute sulfuric acid pre-wash of the carbon bead sorbent was performed when preparing the in-house tubes.

This method was evaluated when the OSHA Time Weighted Average (TWA) Permissible Exposure Limit (PEL) for ammonia was 50 ppm. As of this writing, the OSHA Final Rule Limit for exposure to ammonia is now a Short-Term Exposure Limit (STEL) of 35 ppm.

The method has been validated for TWA samples using sampling flow rates of about 0.10 liter per minute (L/min) and sampling times of 3 to 4 h. An evaluation of four types of ammonia detector tubes was carried out simultaneously with the method validation. The results of the detector tube study are reported in OSHA Product Evaluation No. 7 (10.3). A preliminary test was also conducted on ammonia dosimeter tubes obtained from Wilson Safety Products (Reading, PA). The testing of the dosimeter tubes was discontinued since these tubes could not measure concentrations above 50 ppm ammonia during the experiments.

The validation of OSHA Method No. ID-188 (10.1) consisted of the following experimental protocol:

1. Analysis of spiked samples.
2. Analysis of dynamically generated samples having concentrations of approximately 0.5, 1, and 2 times the TWA PEL. Test atmospheres were generated using 50% RH and 25 °C.
3. Collection efficiency and breakthrough studies of the CISA sampling tubes.
4. Determination of the storage stability of ammonia collected with CISA tubes.
5. Determination of any variation in results when sampling at high and low RH.
6. Comparison of the ion chromatographic method with the ISE method for the determination of ammonia in workplace atmospheres.
7. Determination of the qualitative and quantitative detection limits.
8. Collection and analysis of ammonia samples employing Supelco tubes and comparison with tubes produced in-house.

A generation system, shown in Figure 1, was used for simultaneous testing of detector tubes and continual sampling devices. All generations of ammonia test atmospheres, and hence all experiments, with two exceptions, were performed using the apparatus shown in Figure 1. The analysis and detection limit studies did not use test atmospheres; these samples were spiked with solutions of ammonium sulfate.

### Ammonia Gas Concentration

Ammonia in nitrogen (certified standard, 0.99% ammonia, Air Products Co., Long Beach, CA) was used as the contaminant source. The concentration of ammonia in the cylinder was verified by the following technique:

- a. The undiluted gas stream from the cylinder was sampled with a gas syringe and then injected into 0.1 N sulfuric acid contained in septum-capped vials.
- b. These samples were analyzed for ammonia with an Orion Model 9512 Ammonia Ion Specific Electrode (ISE) and an Orion Model EA940 IonAnalyzer (10.4). The results are shown below:

Theoretical NH <sub>3</sub>	Found NH <sub>3</sub> (µg) Spikes (µg)	Recovery %	SD	CV
60.5	56.8	93.9		
60.5	59.8	99.8		
60.5	54.2	89.6		
60.5	50.2	83.0		
			6.70	0.073
Average		91.3		

The ammonia aliquot results were compared to the manufacturer's stated concentration value. The average spiked sample recovery was 91.3% of the stated value and the CV was 0.073. The manufacturer's stated value was used for all calculations. The lower recoveries were considered to be due to variability in analysis and not due to a change in the stated cylinder concentration. The ISE method has displayed a significant amount of variability in results and slightly lower than expected recoveries. Internal quality control data and results of ISE samples generated during this evaluation are evidence of this variability and decreased recovery when using the ISE method.

### Generation System Components

The ammonia gas was mixed, using a glass mixing chamber, with filtered, tempered air. A flow, temperature and humidity control system (Miller-Nelson Research Inc., Model HCS-301) was used to condition the diluent air for mixing. Moisture and other contaminants were removed from the diluent air by using a charcoal, molecular sieve and Drierite filtering system. A Teflon sampling manifold and connections were attached to the mixing chamber. Diluent air flow was determined using a dry test meter (Singer Co., Model No. DTM 115) before, during, and after each experiment. Ammonia flow rates were controlled by a mass flow controller (Tylan Model FC 260), and were measured before and after each experiment with a soap bubble flow-meter. During each experiment the flow rate was monitored using the readout (LED display) for the mass flow controller.

### Sample Collection

Air samples were collected from the manifold using Du Pont Model P125 pumps (Du Pont Co. Wilmington, DE) calibrated at flow rates of about **0.1 L/min** for all generation experiments. Specific sampling times are mentioned in the procedures for each experiment.

## Sample Analysis

Samples, blanks and prepared standards were analyzed for ammonium ion by ion chromatography (10.1). Analyses and data reduction were performed using a Dionex Model 2010i Ion Chromatograph interfaced to a Hewlett-Packard 3357 Laboratory Automation System. An IBM AT Personal Computer with Autolon 400 software was used during later analyses. All sample results were calculated using a concentration-response curve with peak areas used for signal measurement. Sample results were statistically examined for outliers and homogeneous variance. Possible outliers were determined using the American Society for Testing and Materials (ASTM) test for outliers (10.5). Homogeneity of the coefficients of variation was determined using the Bartlett's test (10.6).

### 1. Analysis (Spiked Samples)

**Procedure:** Twenty-one spiked samples (7 samples at each test level) were prepared and analyzed. The spiked concentrations correspond to approximately 0.5, 1 and 2 times the TWA PEL when using a 24-L air volume. Recoveries represent the desorption efficiency and also provide precision and accuracy data for the analytical portion of the method.

1.1. Three sets of spiked samples were prepared using the following procedure:

1.1.1. A concentrated solution of ammonium sulfate  $[(\text{NH}_4)_2\text{SO}_4]$  was prepared by dissolving a weighed amount of  $(\text{NH}_4)_2\text{SO}_4$  ("Baker Analyzed" Reagent, ACS) in deionized water (DI  $\text{H}_2\text{O}$ ).

1.1.2. Aliquots of this solution were injected into in-house prepared sorbent tubes using a calibrated micropipette.

1.1.3. Sufficient  $(\text{NH}_4)_2\text{SO}_4$  solution was added so that the tubes in each set would contain an amount of ammonia expected after collection from atmospheres at approximately 0.5, 1, and 2 times the PEL, respectively.

1.1.4. The spiked tubes were allowed to stand overnight at room temperature.

1.2. The carbon beads were removed from each tube and desorbed with DI  $\text{H}_2\text{O}$  and analyzed as mentioned in the method (10.1). The glass tube was also rinsed with DI  $\text{H}_2\text{O}$ . Blanks were also prepared in the same fashion.

**Results:** The results are given in Table 1. All data were used except for one sample (2 x TWA PEL) which appeared contaminated with an unknown substance and gave baseline irregularities during analysis. All results passed the outlier and Bartlett's tests and were pooled. The analytical coefficient of variation ( $\text{CV}_1$ ) was 0.031 and recovery was 99.7%.

### 2. Sampling and Analysis

**Procedure:** Twenty-four samples were taken from the dynamic generation system mentioned in the Introduction. Sample results from the dynamic system provide the overall error and precision of the sampling and analytical method. Overall error (OE) should be within  $\pm 25\%$  and is calculated using the following equation (10.7):

$$\text{Overall Error} = \pm [|\text{mean bias}| + 2\text{CV}_T] \times 100\%$$

2.1. Samples were collected from gas streams (50% RH and  $25^\circ\text{C}$ ) containing ammonia at approximately 0.5, 1, and 2 times the TWA PEL.

- 2.2. In-house prepared tubes containing beaded activated carbon with 5% (by weight) sulfuric acid as described in the method (10.1) and similar tubes prepared by Supelco were taken side-by-side.
- 2.3. Two to four samples were collected during each generation experiment. Three to four samples were desired, but in several cases pump failure ended the determination.
- 2.4. Collection rates were about 0.1 L/min. Collection times were 3 to 4 h.
- 2.5. Samples were desorbed with 50 or 100 mL of DI H<sub>2</sub>O and analyzed.

**Results:** Sample results are listed in Table 2 and are only for the in-house tubes. Supelco tube results are similar. The in-house tube samples collected at 50% RH (Table 2) show good precision and accuracy. The total coefficient of variation (CV<sub>T</sub>) was 0.050 and the OE (total) was ±10.9%. Bias was less than 1%.

### 3. Collection Efficiency and Breakthrough Studies

#### 3.1. Collection Efficiency

**Procedure:** Test atmospheres were generated and samples were taken to measure the sorbent collection efficiency at the upper concentration limit of the validation.

3.1.1. A determination of the collection efficiency was performed using five Supelco tubes in which ammonia at 2 times the TWA PEL was collected. Two samples were collected at 30% and three samples at 80% RH. Samples were taken for approximately 200 min. The amounts of ammonia collected in the first and second sections of the tubes were determined.

3.1.2. The collection efficiency was calculated by dividing the amount collected in the first section by the total amount of ammonia collected in the first and second sections.

**Results:** The results are given in Table 3. The collection efficiency was 100%. No ammonia was detected in the backup sections. The results indicate that the collection efficiency is excellent.

#### 3.2. Breakthrough

**Procedure:** Samples were generated at a concentration greater than the validation level to determine the extent of breakthrough from the first solid sorbent section into a second section.

3.2.1. The possibility of breakthrough of ammonia during sampling was examined by collecting six samples at approximately 5 times the TWA PEL for 335 min, using Supelco tubes. Generation conditions were 50% RH and 25 °C.

3.2.2. The main sections were each desorbed in 250 mL of DI H<sub>2</sub>O. To facilitate detection of any breakthrough, the backup sections were each desorbed in 10 mL of DI H<sub>2</sub>O.

**Results:** The results given in Table 3 show the overall recovery was 94.6% and the CV was 0.032. Ammonia was not detected in the backup sections, indicating no evidence of breakthrough.

### 4. Storage Stability of Ammonia Samples Collected on CISA

**Procedure:** A long-term evaluation of sample media stability was done to assess any potential problems if delays in sample analyses occur.

- 4.1. Supelco tube samples were collected from a gas stream adjusted to 50% RH, 25 °C and an ammonia concentration of approximately 50 ppm.
- 4.2. A collection time of about 3.5 h was used.
- 4.3. Samples were capped and stored for various periods up to 29 days before preparation and analysis. Samples were stored in a desk drawer.

**Results:** The results given in Table 4 indicate a slight loss of ammonia (<10%) during approximately one month of storage. The slight decrease in recovery does not appear detrimental to the overall accuracy of the method. Samples can be stored for at least 29 days before analysis.

## 5. Humidity Tests

**Procedure:** Samples were collected at high (80%) and low (30%) RH using similar conditions mentioned in Section 2, where samples were collected at 50% RH. Supelco and in-house tubes were taken side-by-side. Sample recoveries for these three humidity levels were examined to determine any significant differences.

**Results:** The low and high RH results are given in Table 5; the 50% RH results are shown in Table 2. Results listed are for in-house tubes only. Supelco tubes gave similar results. Sampling at different humidities displayed no apparent effect on recovery. An analysis of variance (F test) was performed on the data to determine any significant difference among or within the different humidity groups. Variance at each concentration level (0.5, 1, and 2 times the TWA PEL) was compared across the 3 humidity levels (25-30, 50, and 80% RH). The variance among and within the different concentration groups gave acceptable calculated F values with the exception of the data at the TWA PEL. At this concentration only three samples were collected at the low humidity level; these recoveries were lower than expected and appeared to be due to a dilution problem during ammonia generation. The reference method bubbler samples taken side-by-side also gave lower than expected results. The test at low RH was one of the first experiments conducted. This anomalous behavior was not observed for any of the other data.

The recoveries across the 3 different humidity levels were also considered. No evidence of any significant constant increase or decrease in average recovery was apparent when generation data are compared at different humidity levels. Therefore, the data indicate no apparent humidity effect on recovery.

## 6. Method Comparison

**Procedure:** The CISA sampling and ion chromatography (IC) analytical method was compared to a reference method to determine if any significant disagreement existed between the two methods. The bubbler sampling and ISE analytical method (10.4) was chosen as the reference method. The comparison was conducted as described below:

- 6.1. Side-by-side samples of CISA tubes (both commercial and in-house tubes) and bubblers containing 0.1 N sulfuric acid were collected at 25 °C and 25-30%, 50%, and 80% RH. Du Pont Model P4000 pumps were used to collect bubbler samples. Bubbler collection rates were 1 L/min and collection times were 3 to 4 h. The bubbler solutions were analyzed using an Orion Model 9512 Ammonia ISE and an Orion Model EA940 IonAnalyzer (10.4).
- 6.2. The CISA tubes were sampled and analyzed using the procedures described in the Introduction.

**Results:** The results are given in Table 6. Each CISA and bubbler sample value listed is an average value of two to four samples. Each comparison is for samples collected side-by-side. Statistical treatments are also given. Each sample comparison is based on the averages of the CISA and bubbler samples collected side-by-side. Linear regression comparison calculations are also given. The results of the two methods show the CISA sampling and corresponding IC analytical method has an overall positive bias of approximately 7% (slope =  $1.07 \pm 0.0387$ ) when compared to the bubbler method. Complete listings of individual CISA and bubbler sample results are given in the Appendix.

## 7. Analytical Detection Limits

**Procedure:** The qualitative detection limit for the analysis of ammonia by IC was calculated using the Rank Sum Test (10.8). A modification or derivation of the International Union of Pure and Applied Chemistry (IUPAC) detection limit equation (10.9) was used to determine the quantitative detection limit. At the sensitivity level tested, blank readings and the standard deviation of the blank were equal to zero. The lack of a blank signal does not satisfy a strict interpretation of the IUPAC detection limit when using the equation shown in Table 7. The quantitative detection limit for this method is calculated using the standard deviation of a standard below the range of the expected detection limit as a substitute for the blank readings. The procedure used for sample preparation to determine detection limits is discussed below:

- 7.1. Low concentration ammonia samples were prepared from an ammonium chloride solution (1,000  $\mu\text{g/mL}$  as  $\text{NH}_3$ ). The sample concentrations were 0.05, 0.1, 0.2, and 0.5  $\mu\text{g/mL}$  ammonia.
- 7.2. All solutions were made in 0.005 N sulfuric acid. This is the concentration expected when a typical 500-mg section of acid-treated carbon beads from a sample tube is desorbed with 100 mL of DI  $\text{H}_2\text{O}$ .
- 7.3. A blank sample was prepared containing the same sulfuric acid concentration as the ammonia samples.
- 7.4. Samples were analyzed by IC with a 50- $\mu\text{L}$  sample loop and 30-microsiemens detector setting.

**Results:** The qualitative and quantitative detection limits (Table 7) are 0.20 and 0.50  $\mu\text{g NH}_3/\text{mL}$  solution, respectively. Using a 24-L air volume and a 50-mL sample volume, the qualitative limit is 0.60 ppm and the quantitative limit is 1.5 ppm ammonia in air. For a 7.5-L air sample, these limits are 1.9 and 4.8 ppm, respectively.

## 8. Collection of Ammonia Samples - Supelco Tubes

**Procedure:** Experiments were done with in-house sampling tubes and tubes prepared by Supelco. Side-by-side sampling at varied humidity and concentration levels was performed to compare both tubes. Recoveries were compared and a t-test was used to determine if any significant difference in results existed between the two tubes (10.10).

**Results:** The results are shown in Table 8. Separate Supelco tube results are also shown in Table 8. The results indicate the two different sets of tubes compare well with each other in their ability to collect and retain ammonia. A t-test (10.10) showed no significant difference between recoveries for the two different sets of tubes.



The backup sections of the Supelco tubes were also analyzed. All backup results were non-detected when the samples were analyzed shortly after desorption. A very small peak eluting at the same time as ammonia developed after solutions stood for 1 week.

## 9. Conclusions

The sample determinations shown in Tables 1 and 2 are well within NIOSH or OSHA accuracy and precision guidelines (10.6, 10.7). Collection efficiency, breakthrough, and storage stability are adequate. A humidity effect was not noted. The comparison of the bubbler with the IC method showed a positive linear regression slope of 1.07. This is to be expected since overall recoveries of the bubbler method were about 9% lower than expected (theoretical) and IC sample recoveries exhibited minimal bias. The sampling and analysis data for bubbler samples (three different RH and concentration levels) gave an overall recovery of 91.0% and a CV of 0.091. In general, the lowest recoveries for the bubbler samples were measured during preliminary experiments before improvements were made in the ISE procedure. Results for all samples taken and analyzed by IC or ISE are shown in the Appendix.

Detection limits are adequate for 4-h exposure determinations. For STEL measurements, larger sample volumes will need to be taken over the 15-min sampling period. It is recommended to use 0.5 L/min for STEL assessments (total air volume = 7.5 L). Although no STEL experiments were performed during this evaluation, a literature reference (10.2) experiment conducted at a sampling rate of 0.5 L/min for 12 min at a concentration of 25 ppm indicated no detectable breakthrough. The experimenters also indicated the theoretical capacity of the sampling tube is 8.5 mg ammonia.

The method for collecting ammonia with CISA tubes and analysis by IC is a precise and accurate method for the determination of ammonia in workplace atmospheres.

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Table 1  
Analysis - Spiked NH<sub>3</sub> Samples

(OSHA-TWA PEL)*							
µg NH <sub>3</sub> Taken	µg NH <sub>3</sub> Found	F/T	n	Mean	Std Dev	CV	AE
<u>(0.5 x TWA PEL)</u>							
348.0	341.0	0.9799					
348.0	361.0	1.0374					
348.0	342.0	0.9828					
348.0	326.0	0.9368					
348.0	338.0	0.9713					
348.0	339.0	0.9741					
348.0	358.0	1.0287					
			7	0.987	0.035	0.035	8.3
<u>(1 x TWA PEL)</u>							
818.0	841.0	1.0281					
818.0	855.0	1.0452					
818.0	825.0	1.0086					
818.0	828.0	1.0122					
818.0	830.0	1.0147					
818.0	848.0	1.0367					
818.0	872.0	1.0660					
			7	1.030	0.021	0.020	7.1
<u>(2 x TWA PEL)</u>							
1636.0	1540.0	0.9413					
1636.0	1610.0	0.9841					
1636.0	1543.0	0.9432					
1636.0	1674.0	1.0232					
1636.0	1609.0	0.9835					
1636.0	1536.0	0.9389					
			6**	0.969	0.034	0.035	10.1
F/T	= Found/Taken						
AE	= Analytical Error (± %)						

Bias = -0.003

CV<sub>1</sub> (pooled) = 0.031

Analytical Error  
(Total) = ±6.5%

\* Levels are approximate.

\*\* Seven samples were taken; however, one sample was omitted due to baseline irregularities occurring during analysis.

Table 2  
 Sampling and Analysis  
 (50% RH and 25 °C)

(OSHA-TWA PEL)							
ppm NH <sub>3</sub> Taken	ppm NH <sub>3</sub> Found	F/T	n	Mean	Std Dev	CV	OE
<u>(0.5 x TWA PEL)</u>							
34.2	35.1	1.0263					
34.2	36.1	1.0556					
34.2	39.6	1.1579					
30.7	29.8	0.9707					
30.7	29.5	0.9609					
			5	1.034	0.079	0.077	18.8
<u>(1 x TWA PEL)</u>							
45.4	49.2	1.0837					
45.4	46.9	1.0330					
45.4	47.4	1.0441					
50.3	47.0	0.9344					
50.3	47.6	0.9463					
50.3	48.2	0.9583					
50.1	51.2	1.0220					
50.1	50.3	1.0040					
50.1	872.0	1.0180					
			9	1.005	0.049	0.049	10.3
<u>(2 x TWA PEL)</u>							
100.7	94.9	0.9424					
100.7	94.5	0.9384					
100.7	91.9	0.9126					
100.7	97.6	0.9756					
98.5	96.1	0.9835					
98.5	97.8	0.9929					
98.5	93.5	0.9841					
101.8	98.5	0.9676					
101.8	95.9	0.9420					

101.8	1609.0	0.9835						
			10	0.957	0.025	0.026	9.4	

---

F/T	= Found/Taken
OE	= Analytical Error ( $\pm$ %)
Bias	= -0.009
CV <sub>2</sub> (pooled)	= 0.048
Overall Error	= $\pm$ 10.5%
CVT (pooled)	= 0.050
Overall Error (Total)	= $\pm$ 10.5%

Table 3  
Collection Efficiency and Breakthrough Collection Efficiency –  
Supelco Tubes 50 % RH and 25 °C

Sample	ppm	Collection		ppm Ammonia Found		Collection
No.	Ammonia	RH (%)	Time (min)	1st Sec.	2nd Sec.	Eff. (%)
1	99.5	30	190	87.8	ND	100
2	99.5	30	190	91.6	ND	100
3	101.3	80	215	103.4	ND	100
4	101.3	80	215	105.5	ND	100
5	101.3	80	215	102.8	ND	100

Samples were collected at approximately 0.1 L/min flow rate. ND = None detected. Detection limit = 1.5 ppm NH<sub>3</sub>

Breakthrough - Supelco Tubes 50% RH and 25 °C

µg	NH <sub>3</sub> Found		NH <sub>3</sub> Taken	% Recovery
	Air Vol (L)	ppm	ppm	
5189	29.52	252	258	
5012	29.83	241	258	
5218	29.27	256	258	
4968	29.61	241	258	
4802	28.79	239	258	
5426	32.94	236	258	
n = 6				94.6
mean = 244				
Std Dev = 7.94				
CV = 0.032				

Samples were collected at about 0.1 L/min for 335 min at approximately 5 x TWA PEL. No ammonia was detected in the backup sections.

Table 4  
Storage Stability Test - 1 x TWA PEL, 50 % RH, 25 °C

Storage Day	µg	Air Vol (L)	Found ppm NH <sub>3</sub>	Taken ppm NH <sub>3</sub>	% Recovery
<u>Day 1</u>	705.3	18.70	54.1	53.3	
	606.7	16.83	52.4	53.3	
	705.3	18.70	54.1	53.3	
		n	3		
		mean	53.1		100
		Std Dev	0.907		
		CV	0.017		
<u>Day 5*</u>	672.2	19.26	50.1	53.3	
	620.8	16.54	53.9	53.3	
			n	2	
		mean	52.0		98
		Std Dev	2.69		
		CV	0.052		
<u>Day 9</u>	614.0	17.64	50.0	53.3	
	609.6	17.50	50.0	53.3	
	555.2	17.04	46.8	53.3	
		n	3		
		mean	48.9		92
		Std Dev	1.85		
		CV	0.038		
<u>Day 15</u>	664.4	18.37	51.9	53.3	
	609.6	18.29	47.8	53.3	
	661.0	19.05	49.8	53.3	
		n	3		
		mean	49.8		93
		Std Dev	2.05		



			CV	0.041		
<u>Day 29</u>	570.4	17.03		48.1	50.1	
	536.4	15.98		48.2	50.1	
	546.3	16.62		47.2	50.1	
			n	3		
			mean	47.8		95
			Std Dev	0.551		
			CV	0.012		

---

\* One result was deleted due to pump failure. All samples were collected using Supelco tubes. Some of the sampling tubes used had been stored 11 months prior to use. Storage times reported are from the day of collection to the day of analytical preparation.

Table 5  
NH<sub>3</sub>-IC Humidity Study

(OSHA-TWA PEL)							
ppm NH <sub>3</sub> Taken	ppm NH <sub>3</sub> Found	F/T	n	Mean	Std Dev	CV	OE
<u>25-30% RH and 25 °C</u>							
<u>(0.5 x TWA PEL)</u>							
34	28.7	0.8441					
34	29.4	0.8647					
34	29.6	0.8706					
34.3	34.0	0.9913					
34.3	31.9	0.9300					
34.3	31.3	0.9125					
24.3	24.4	1.0041					
24.3	23.5	0.9671					
24.3	23.1	0.9506					
			9	0.926	0.057	0.062	19.8
<u>(1 x TWA PEL)</u>							
55.0	44.8	0.8145					
55.0	43.0	0.7818					
55.0	46.5	0.8455					
			3	0.814	0.032	0.039	26.4
<u>(2 x TWA PEL)</u>							
99.6	90.0	0.9036					
99.6	95.0	0.9538					
99.6	94.6	0.9498					
99.6	101.8	1.0231					
99.6	101.4	1.0191					
99.6	100.4	1.0090					
			6	0.976	0.048	0.049	12.2
F/T	= Found/Taken						
OE	= Overall Error (± %)						
Bias	= -0.076						
CV <sub>2</sub> (pooled)	= 0.055						

Overall Error (Total) = ±18.7%

80% RH and 25 °C

(0.5 x TWA PEL)

29.2	27.3	0.9349					
29.2	28.6	0.9795					
29.2	29.0	0.9932					
29.2	22.1	0.9132					
29.2	22.2	0.9174					
29.2	22.3	0.9215					
			6	0.943	0.943	0.036	13.0

(1 x TWA PEL)

50.2	48.4	0.9641					
50.2	47.0	0.9363					
50.2	49.1	0.9781					
48.1	41.6	0.8649					
48.1	45.6	0.9480					
48.1	40.9	0.8503					
			6	0.924	0.053	0.058	19.2

(1 x TWA PEL)

101.3	105.8	1.0444					
101.3	98.0	0.9674					
101.3	102.6	1.0128					
			3	1.008	0.039	0.038	8.5

F/T = Found/Taken

OE = Overall Error (± %)

Bias = -0.052

CV<sub>2</sub> (pooled) = 0.047

Overall Error (Total) = ±14.5%

---

Table 6  
Comparison of Sampling and Analytical Methods

RH	IC Found (ppm)	ISE Found (ppm)	RR
25-30%			
	29.2	29.7	0.983
	32.4	28.6	1.133
	23.7	22.9	1.035
	44.8	44.4	1.009
	93.2	88.9	1.048
	101.2	94.4	1.072
50 %			
	36.9	29.1	1.268
	29.7	29.2	1.017
	47.8	44.9	1.065
	47.6	42.5	1.120
	50.9	53.3	0.955
	94.7	88.7	1.068
	95.8	79.3	1.208
	98.2	99.7	0.985
80%			
	28.3	25.3	1.119
	22.2	23.0	0.965
	48.1	46.4	1.037
	42.7	46.2	0.924
	102.1	92.1	1.109

RR = Relative Recovery = IC Found/ISE Found Each comparison listed is the average value for all CISA and bubbler samples collected side-by-side for a given experiment. IC samples were collected using CISA tubes and analyzed by ion chromatography. ISE samples were collected using bubblers containing 0.1 N H<sub>2</sub>SO<sub>4</sub> and analyzed by ISE.

Linear Regression Comparison (all analyses)

Correlation Coefficient (r) = 0.9890  
 Slope (b) = 1.0698  
 Intercept (a) = -0.5028  
 Std Dev of Slope (Sb) = 0.0387

Table 7  
Determination of Qualitative Detection Limit

µg/mL NH <sub>3</sub>	Integrated Area/1000
BLANK	0, 0, 0, 0, 0, 0
0.050	0, 0, 0, 0, 0, 0
0.100	0, 0, 1.202, 1.238, 1.015, 1.314
0.200	2.314, 2.571, 2.739, 3.033, 2.897, 2.886
0.500	6.403, 6.934, 7.515, 7.306, 7.975, 8.667
<b>Rank Sum</b>	
a	= 0.01 (two-tailed test)
n <sub>1</sub>	= 6 (no. of 0.200 µg/mL determinations)
n <sub>2</sub>	= 6 (no. of blank determinations)
n	= n <sub>1</sub> + n <sub>2</sub> = 12
R	= 69 (sum of ranks for 0.200 µg/mL)
R <sub>n</sub>	= n <sub>1</sub> (n + 1) - R = 9
R <sub>(table)</sub>	= 23

Therefore, R<sub>n</sub> is not equal to or greater than R<sub>(table)</sub>, and both sample populations are significantly different. Qualitative detection limit = 0.20 µg ammonia per mL, or 10.0 µg in a 50-mL sample volume. This corresponds to a 0.60 ppm ammonia for a 24-L air volume.

Determination of Quantitative Detection Limit

Ammonia (as NH<sub>3</sub>) (µg/mL)

Sample No.	0.100 PA	0.200 PA	0.500 PA
1	0	2.314	6.403
2	0	2.571	6.934
3	1.202	2.739	7.515
4	1.238	3.033	7.306
5	1.015	2.897	7.975
6	1.314	2.886	8.667
n	6	6	6
Mean	0.795	2.740	7.467
Std Dev	0.623	0.261	0.793
CV <sub>2</sub>	0.784	0.095	0.106

PA = Integrated Peak Area (NH<sub>3</sub>)/1000

IUPAC Method

Using the equation:  $C_{ld} = k(sd)/m$

Where:

$C_{ld}$  = the smallest detectable concentration an analytical instrument can determine at a given confidence level.

k = 10, thus giving 99.99% confidence that any detectable signal will be greater than or equal to an average blank or low standard reading plus ten times the standard deviation.

sd = standard deviation of blank or low standard readings.

m = analytical sensitivity or slope as calculated by linear regression.

Minimum detectable signal:

$$C_{ld} = 10(0.623)/0.01238$$

$$C_{ld} = 378 \text{ ppb} = 0.50 \text{ µg/mL}$$

The quantitative detection limit = 0.50 µg ammonia per mL, or 25 µg in a 50-mL sample volume. This corresponds to a 1.5 ppm ammonia concentration for a 24-L air volume.

Table 8

## Side-by-Side Comparison of Supelco Tubes and In-house Carbon Bead Tubes

Level	RH	ppm NH <sub>3</sub> Found, Lab Prep	ppm NH <sub>3</sub> Found, Supelco
<u>0.5 x TWA PEL</u>	25	24.4	23.4
		23.5	24.1
		23.1	23.4
Mean		23.7	23.6
Std Dev		0.666	0.404
CV <sub>2</sub>		0.028	0.017
ppm taken		24.3	24.3
% recovered		97.5	97.1
<u>0.5 x TWA PEL</u>	80	22.1	19.9
		22.2	20.6
		22.3	20.2
Mean		22.2	20.2
Std Dev		0.100	0.351
CV <sub>2</sub>		0.005	0.017
ppm taken		24.2	24.2
% recovered		91.7	83.5
<u>1 x TWA PEL</u>	30	44.8	48.4
		43.0	47.6
		46.5	48.8
Mean		44.8	48.3
Std Dev		1.750	0.611
CV <sub>2</sub>		0.039	0.013
ppm taken		55.0	55.0
% recovered		81.5	87.8
<u>1 x TWA PEL</u>	50	51.2	48.1
		50.3	48.2
		51.0	47.2
Mean		50.9	47.8
Std Dev		0.473	0.551

CV <sub>2</sub>		0.009	0.012
ppm taken		50.1	50.1
% recovered		101.6	95.4
<u>2 x TWA PEL</u>	30	101.8	87.8
		101.4	91.6
		100.4	
Mean		101.2	89.7
Std Dev		0.721	2.69
CV <sub>2</sub>		0.007	0.030
ppm taken		99.5	99.5
% recovered		101.7	90.1
<u>2 x TWA PEL</u>	80	105.8	103.4
		98.0	105.5
		102.6	102.8
Mean		102.1	103.9
Std Dev		3.92	1.418
CV <sub>2</sub>		0.038	0.014
ppm taken		101.3	101.3
% recovered		100.8	102.6

---

t-test comparison: A student t-test calculation was carried out comparing the individual Supelco tube recoveries with the individual in-house tube recoveries. These samples were taken side-by-side.

$$t_{\text{calc}} = 1.129 \quad \text{df} = 33$$

$$t_{\text{Table}} = 2.750 \quad (\text{p} < 0.01) \quad \text{df} = 30 \quad (\text{2-tailed})$$

$$t_{\text{Table}} = 2.704 \quad (\text{p} < 0.01) \quad \text{df} = 40 \quad (\text{2-tailed})$$

The calculated value for t was less than the Table values. Therefore, the Supelco and in-house tube results are likely from the same population, and compare well with each other.



NH<sub>3</sub>-Supelco Tubes  
All RH Levels

(OSHA-TWA PEL)							
ppm NH <sub>3</sub> Taken	ppm NH <sub>3</sub> Found	F/T	n	Mean	Std Dev	CV	OE
(0.5 x TWA PEL)							
24.3	23.4	0.9630					
24.3	24.1	0.9918					
24.3	23.4	0.9630					
24.2	19.9	0.8223					
24.2	20.6	0.8512					
24.2	20.2	0.8347					
			6	0.904	0.076	0.084	26.4
(1 x TWA PEL)							
55.0	48.4	0.8800					
55.0	47.6	0.8655					
55.0	48.8	0.8873					
50.1	48.1	0.9601					
50.1	48.2	0.9621					
50.1	47.2	0.9421					
			6	0.916	0.043	0.047	17.9
(2 x TWA PEL)							
99.5	87.8	0.8824					
99.5	91.6	0.9206					
101.3	103.4	1.0207					
101.3	105.5	1.0415					
101.3	102.8	1.0148					
			5	0.976	0.070	0.072	16.8
F/T	= Found/Taken						
OE	= Overall Error (± %)						
Bias	= -0.070						
CV <sub>2</sub> (pooled)	= 0.069						
Overall Error (Total)	= ±20.9%						

### Dynamic Generation System for Production of Ammonia Atmospheres

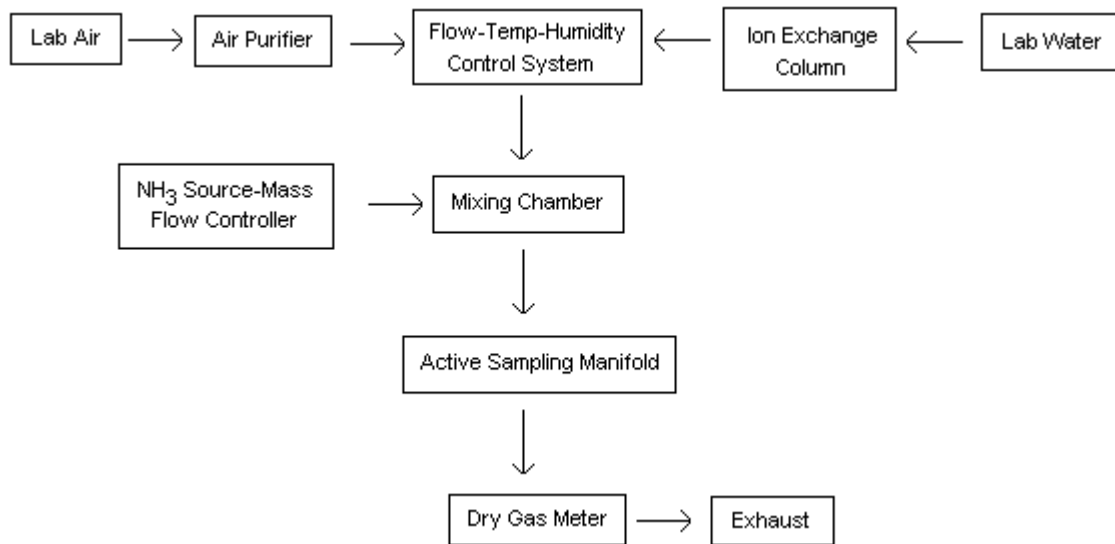


Figure 1

Appendix  
NH<sub>3</sub>-IC (All Data) Results

(OSHA-TWA PEL)

ppm NH <sub>3</sub> Taken	ppm NH <sub>3</sub> Found	F/T	n	Mean	Std Dev	CV	OE
<u>(0.5 x TWA PEL)</u>							
34.0	28.7	0.8441					
34.0	29.4	0.8647					
34.0	29.6	0.8706					
34.3	34.0	0.9913					
34.3	31.9	0.9300					
34.3	31.3	0.9125					
24.3	24.4	1.0041					
24.3	23.5	0.9671					
24.3	23.1	0.9506					
34.2	35.1	1.0263					
34.2	36.1	1.0556					
34.2	39.6	1.1579					
30.7	29.8	0.9707					
30.7	29.5	0.9609					
29.2	27.3	0.9349					
29.2	28.6	0.9795					
29.2	29.0	0.9932					
24.2	22.1	0.9132					
24.2	22.2	0.9174					
24.2	22.3	0.9215					
			20	0.958	0.071	0.075	19.1

(1 x TWA PEL)

55.0	44.8	0.8145
55.0	43.0	0.7818
55.0	46.5	0.8455
45.4	49.2	1.0837
45.4	46.9	1.0330
45.4	47.4	1.0441

50.3	47.0	0.9344
50.3	47.6	0.9463
50.3	48.2	0.9583
50.1	51.2	1.0220
50.1	50.3	1.0040
50.1	51.0	1.0180
50.2	48.4	0.9641
50.2	47.0	0.9363
50.2	49.1	0.9781
48.1	41.6	0.8649
48.1	45.6	0.9480
48.1	40.9	0.8503

18 0.946 0.085 0.090 23.3

(2 x TWA PEL)

99.6	90.0	0.9036
99.6	95.0	0.9538
99.6	94.6	0.9498
99.5	101.8	1.0231
99.5	101.4	1.0090
99.5	100.4	0.9424
100.7	94.9	0.9384
100.7	94.5	0.9126
100.7	91.9	0.9692
100.7	97.6	0.9756
98.5	96.1	0.9929
98.5	97.8	0.9492
98.5	93.5	0.9676
101.8	98.5	0.9420
101.8	95.9	0.9843
101.8	100.2	1.0444
101.3	105.8	0.9674
101.3	98.0	1.0128
101.3	102.6	

19 0.971 0.038 0.039 10.7

---

F/T	= Found/Taken
OE	= Overall Error ( $\pm$ %)
Bias	= -0.041
CV <sub>2</sub> (pooled)	= 0.071
Overall Error (Total)	= $\pm$ 18.3%

NH<sub>3</sub>-ISE (All Data) Results

(OSHA-TWA PEL)

ppm NH <sub>3</sub> Taken	ppm NH <sub>3</sub> Found	F/T	n	Mean	Std Dev	CV	OE
<u>(0.5 x TWA PEL)</u>							
34.0	29.0	0.8529					
34.0	30.4	0.8941					
34.3	29.0	0.8455					
34.3	27.4	0.7988					
34.3	29.3	0.8542					
24.3	22.6	0.9300					
24.3	23.0	0.9465					
24.3	22.8	0.9383					
24.3	23.3	0.9588					
34.2	29.4	0.8596					
34.2	29.4	0.8596					
34.2	28.4	0.8304					
30.7	30.3	0.9870					
30.7	28.9	0.9414					
30.7	28.4	0.9251					
29.2	24.6	0.8425					
29.2	25.3	0.8664					
29.2	26.2	0.8973					
24.2	23.2	0.9587					
24.2	23.5	0.9711					
24.2	22.2	0.9174					
24.2	22.3	0.9587					

22 0.902 0.054 0.059 21.7

(1 x TWA PEL)

55.0	42.7	0.7764
55.0	46.3	0.8418
55.0	45.5	0.8273
55.0	43.1	0.7836
45.4	43.9	0.9670

45.4	51.5	1.1344
45.4	42.2	0.9295
45.4	42.0	0.9251
50.3	42.4	0.8429
50.3	42.5	0.8449
50.1	48.2	0.9621
50.1	53.1	1.0599
50.1	58.6	1.1697
50.2	41.8	0.8327
50.2	48.2	0.9602
50.2	49.1	0.9781
48.1	47.6	0.9896
48.1	44.7	0.9293

18 0.931 0.112 0.120 31.0

(2 x TWA PEL)

99.6	82.1	0.8243
99.6	96.9	0.9729
99.6	87.7	0.8805
99.5	93.6	0.9407
99.5	92.6	0.9307
99.5	97.0	0.9749
100.7	86.6	0.8600
100.7	90.9	0.9027
98.5	84.0	0.8528
98.5	65.5	0.6650
98.5	88.3	0.8964
101.8	98.3	0.9656
101.8	101.2	0.9941
101.3	97.0	0.9576
101.3	86.9	0.8578
101.3	92.3	0.9112

16 0.899 0.080 0.089 28.0

---

F/T = Found/Taken  
 OE = Overall Error (± %)

Bias = -0.090  
CV<sub>2</sub> (pooled) = 0.091  
Overall Error (Total) = ±27.2%