# Sodium Azide and Hydrazoic Acid in Workplace Atmospheres

| | |
|---|---|
| Method no.: | ID-211 |
| Matrix: | Air |
| OSHA Permissible Exposure Limits: | |
| Final Rule Limits: | 0.3 mg/m$^3$ as sodium azide (Ceiling)<br>0.1 ppm as hydrazoic acid (Ceiling)<br>Also Skin Designation |
| Transitional Limit: | None |
| Collection Device: | An air sample is collected using a calibrated sampling pump and a glass tube containing impregnated silica gel (ISG). A pre-filter is used to collect particulate azide. Wipe samples can be taken to determine work surface contamination. |
| Recommended Sampling Rate: | 1 liter per minute (L/min) |
| Recommended Minimum Sampling Time: | 5 minutes |
| Analytical Procedure: | The sampling medium is desorbed using an aqueous solution which contains a mixture of 0.9 mM sodium carbonate ($Na_2CO_3$) and 0.9 mM sodium bicarbonate ($NaHCO_3$). An aliquot of this solution is analyzed as azide ($N_3^-$) by an ion chromatograph equipped with a UV detector. |
| Special Precautions: | Ship samples to the laboratory as soon as possible after collection. Store samples under refrigeration when not in transit. Samples stored at room temperature need to be analyzed within 10 days. |

| | |
|---|---|
| Detection Limit: | |
| Qualitative: | 0.001 ppm as $HN_3$ or 0.003 mg/m$^3$ as $NaN_3$ (5-L air sample) |
| Quantitative: | 0.004 ppm as $HN_3$ or 0.011 mg/m$^3$ as $NaN_3$ (5-L air sample) |
| Precision and Accuracy: | |
| Validation Range: | 0.057 to 2.63 ppm |
| Bias: | -0.022 |
| Overall Error: | ±12.6% |
| $CV_T$ (pooled): | 0.052 |
| Method Classification: | Validated Method |
| Chemist: | James C. Ku |
| Date: | September, 1992 |

*Please note: For problems with accessibility in using figures and illustrations in this method, please contact the author at (801) 233-4900.*



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## 1. Introduction

This method describes the sample collection and analysis of airborne azides [as sodium azide ($NaN_3$) and hydrazoic acid ($HN_3$)]. Air samples are taken in the breathing zone of workplace personnel, and analysis is performed by ion chromatography (IC) with a UV detector.

Note: Hydrazoic acid vapor may coexist with $NaN_3$ in the workplace when $NaN_3$ is handled in the presence of moisture. This method addresses the potential exposure to both substances ($NaN_3$/$HN_3$), and may be extended to include other azide compounds, provided they are soluble in the desorbing solution and collected using the procedure described below. Wipe or bulk samples can also be collected and analyzed using this method.

1.1. History

1.1.1. Various sampling and analysis methods have been proposed in the literature (5.1. - 5.5.) for monitoring azide exposures; however, most lack the sensitivity needed to meet the 0.3 $mg/m^3$ (as $NaN_3$) or 0.1 ppm (as $HN_3$) Ceiling PEL when using short sampling periods. Some of these methods are subject to interferences from many compounds. The ion chromatographic method has interferences from nitrates or bromides. The National Institute of Occupational Safety and Health (NIOSH) had proposed a method for inorganic azide particulates using polyvinyl chloride (PVC) filter collection followed by water extraction and IC determination using sodium bicarbonate/sodium hydroxide eluant (5.6.). To trap any $HN_3$, NIOSH further recommended using a solid sorbent tube containing chromosorb coated with sodium carbonate. The NIOSH method is also subject to interferences and the conductivity detector used lacks sufficient sensitivity for short-term samples.

1.1.2. The OSHA Salt Lake Technical Center (SLTC) previously used a stopgap method for $NaN_3$ (5.7.). Samples were collected with impingers which were inconvenient to use as personal samplers due to possible spillage of the liquid collection solutions or breakage. Other disadvantages are similar to those mentioned above: 1) low sensitivity due to the conductivity detector used; 2) interferences from ions such as bromide, adipic acid, and nitrate.

1.1.3. It was desirable to develop a solid-sorbent sampling and analytical method capable of measuring azide for OSHA compliance purposes. A method was evaluated using a base-impregnated silica gel (ISG) as the collection media. The media is similar to that found in reference 5.5.

1.2. Principle

Particulate $NaN_3$ is collected on a PVC filter or in the glass wool plug of the sampling tube. Gaseous $HN_3$ is collected and converted to $NaN_3$ by the ISG sorbent within the sampling tube. The collected azide on either media is desorbed in a weak buffer solution. The resultant anion, $N_3^-$, is analyzed by IC using a variable wavelength UV detector at 210 nm. A gravimetric conversion is used to calculate the amount of $NaN_3$ or $HN_3$ collected.

1.3. Advantages and Disadvantages

1.3.1. This method has adequate sensitivity to determine compliance with the OSHA Ceiling PEL azide exposures.

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

1.3.3. The potential for sample contamination is minimal. The azide anion, $N_3^-$, is normally not detected in sorbent blanks.

1.3.4. One disadvantage is sample storage stability. Samples should be refrigerated after collection to improve stability. Samples need not be refrigerated during shipment provided they are shipped as soon as possible.

1.3.5. Another disadvantage is the method does not distinguish azide compounds. If other azide compounds are present during sampling, and are soluble in the desorbing solution, positive interferences could occur. However, most industrial operations do not mix different azide-containing compounds in their processes.

1.4. Method Performance

A synopsis of the method performance is presented below. Further information can be found in Section 4.

1.4.1. This method was validated over the concentration range of 0.057 to 0.263 ppm as $HN_3$. An air volume of 5 L and a flow rate of approximately 1 L/min were used.

1.4.2. The qualitative detection limit was 0.00347 $\mu$g/mL or 0.0104 $\mu$g (as $N_3^-$) when using a 3-mL solution volume. This corresponds to 0.001 ppm $HN_3$ or 0.004 mg/m$^3$ $NaN_3$ for a 5-L air volume.

1.4.3. The quantitative detection limit was 0.0116 $\mu$g/mL or 0.0348 $\mu$g (as $N_3^-$) when using a 3-mL solution volume. This corresponds to 0.004 ppm $HN_3$ or 0.011 mg/m$^3$ $NaN_3$ for a 5-L air volume. A 50-$\mu$L sample loop and a detector setting of 0.01 absorbance unit (AU) full-scale output were used.

1.4.4. The sensitivity of the analytical method, when using the instrumental parameters listed in Section 3.7., was calculated from the slope of a linear working range curve (0.1 to 1.0 $\mu$g/mL $N_3^-$). The sensitivity was $2.1 \times 10^7$ area units per 1 $\mu$g/mL. A Dionex Series 4500i ion chromatograph with AI450 computer software was used (Dionex, Sunnyvale, CA).

1.4.5. The precision and accuracy results are shown below (OE = Overall Error):

| | Ceiling |
|---|---|
| CV | 0.052 |

| | |
|---|---|
| Bias | -2.2% |
| OE | ±12.6% |

1.4.6. The collection efficiency at 2 times the PEL was 100%. Samples were collected from a generated test atmosphere of 0.26 ppm $HN_3$ for 5 min.

1.4.7. A breakthrough test was performed at a concentration of 0.9 ppm $HN_3$. Breakthrough was not found when using a sampling time of 30 min and an average sample flow rate of 1 L/min.

1.4.8. Tests indicated the recovery for samples stored at room temperature (20 to 25°C) gradually decreases to between 75 and 80% after 30 days. Slight losses (≈6%) were observed for samples stored 30 days in a refrigerator or freezer.

1.5. Interferences

1.5.1. Other azide compounds will interfere in the analysis of $N_3^-$ if they are collected by the ISG, glass wool, or on the PVC pre-filter. These compounds should normally not exist in industrial operations which specifically use $NaN_3$ or $HN_3$ (i.e. manufacture of air bags, analytical laboratories, etc.).

1.5.2. Any substance that has the same retention time and absorbs UV at 210 nm, when using the ion chromatographic operating conditions described in this method, may be an interference. If the possibility of an interference exists, changing the separation conditions (column, eluant flow rate, eluant concentration, analytical wavelength, etc.) may circumvent the problem.

1.6. Sources of Exposure

Note: Because $NaN_3$ is rapidly converted to $HN_3$ on contact with moisture, $HN_3$ is believed to be the ultimate toxic agent in humans exposed to $NaN_3$ (5.8.).

Sodium azide has been used for a wide variety of military, laboratory, medical, and commercial purposes. While it is not explosive under normal conditions, $NaN_3$ is commonly used in detonators and other explosives. Sodium azide is used extensively as an intermediate in the production of lead azide. The biological uses of azides include inhibition of respiration, differential selection procedures for bacteria, and bacteriocidal agents in diagnostic products (5.9., 5.10.).

Sodium azide is also the chief chemical used to inflate safety airbags in automobiles. Nitrogen gas is produced upon $NaN_3$ detonation. After inflation, a small residue of sodium hydroxide may be left, in addition to lubricants such as corn starch or talc.

1.7. Physical and Chemical Properties (5.11., 5.12.)

Hydrazoic acid (CAS No. 7782-79-8) is a colorless, volatile liquid which is soluble in water. It has a pungent obnoxious odor.

| | |
|---|---|
| Chemical name | Hydrozoic acid |
| Synonym name | Hydrogen azide |
| Chemical formula | $HN_3$ |
| Structural formula | H-N=N≡N |
| Formula weight | 43.03 |
| Freezing point | -80°C |
| Boiling point | 37°C |

Sodium azide (CAS No. 26628-22-8) is a colorless, hexagonal crystalline solid. It is soluble in water or liquid ammonia, slightly soluble in alcohol, and insoluble in ether. It is highly toxic and presents a severe explosion risk when shocked or heated. When heated to 275 to 330°C in dry air, the solid crystals decompose with the evolution of nitrogen gas, leaving a residue of sodium oxide. Sodium hydroxide forms in moist air.

| | |
|---|---|
| Chemical name | Sodium azide |
| Synonym name | Sodium azoimide |
| Chemical formula | $NaN_3$ |
| Structural formula | Na-N=N≡N |
| Formula weight | 65.01 |
| Decomposition temperature | 300°C |
| Specific gravity | 1.846 (@ 20°C) |

1.8. Toxicology (5.13.)

Information listed within this section is a synopsis of current knowledge of the physiological effects of $NaN_3$ and is not intended to be used as a basis for OSHA policy.

Sodium azide/hydrazoic acid is known to produce hypotension (low blood pressure) in laboratory animals and humans, and to form strong complexes with hemoglobin, and consequently block oxygen transport in the blood.

Acute inhalation of $HN_3$ vapor by humans (which forms when $NaN_3$ contacts water) results in lowered blood pressure, eye irritation, bronchitis, headache, weakness, and collapse. A skin designation has been assigned to the OSHA PEL due to the ability of $NaN_3$ to readily penetrate intact skin, and any dermal exposure can significantly contribute to the overall exposure to azide.

## 2. Sampling

2.1. Equipment - Air Samples

2.1.1. Calibrated personal sampling pumps capable of sampling within ±5% of the recommended flow rate of 1 L/min are used.

2.1.2. Solid sorbent sampling tubes containing ISG are prepared by using clean silica gel impregnated with a base.

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The sampling tube is proprietary and is composed of a glass jacket containing a 150-mg ISG front and 75-mg ISG backup section (Cat. No. 226-55, SKC Inc., Eighty Four, PA). The dimensions of the tube are 7-mm o.d., 5-mm i.d., and 70-mm long. The ISG is held in place with glass wool and a stainless steel retainer clip. A pre-filter/cassette sampling assembly should be used with this tube. See Section 2.1.5. for more details regarding the pre-filter.

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2.1.3. A stopwatch and bubble tube or meter are used to calibrate pumps.

2.1.4. Various lengths of polyvinyl chloride tubing are used to connect sampling tubes to pumps.

2.1.5. Anytime the workplace air being sampled is suspected of containing $NaN_3$, use the pre-filter/cassette assembly listed below.

a. PVC membrane filter, 37-mm, 5-mm pore size, [part no. 625413, Mine Safety Appliances (MSA), Pittsburgh, PA or cat. no. P-503700, Omega Specialty Instrument Co., Chelmsford, MA]
b. Polystyrene cassette, 37-mm diameter.
c. Spacer support pad (cat. no. 225-23, SKC Inc.) (use a spacer in place of a backup pad to hold the PVC filter securely in the cassette.)

Assemble the pre-filter and sampling tube such that sampled air enters the cassette first. *Use* *a minimum amount of tubing* to connect the sampling tube to the cassette.

2.1.6. Optional: Desorbing solution (0.9 mM $Na_2CO_3$ + 0.9 mM $NaHCO_3$):

Dissolve 0.191 g $Na_2CO_3$ and 0.151 g $NaHCO_3$ in 2.0 L deionized water.

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Note: This solution is only used if a delay in sample shipment is expected.

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2.2. Equipment - Wipe Samples

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Note: Do not use wipe materials such as smear tabs or those composed of cellulose; preliminary tests indicate azide is unstable on this media (recovery was about 50%). Recoveries of $NaN_3$ spiked on glass fiber or PVC filters were adequate.

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Use either a polyvinyl chloride (PVC) membrane filter, 37-mm, 5-mm pore size, [part no. 625413, Mine Safety Appliances (MSA), Pittsburgh, PA or cat. no. P-503700, Omega Specialty Instrument Co., Chelmsford, MA] or a glass fiber filter, 37-mm, (part no. 61715, Gelman Instrument Company, Ann Arbor, MI). Also see the scintillation vial specification in Section 2.3.

2.3. Equipment - Bulk Samples

Scintillation vials, 20-mL (part no. 74515 or 58515, Kimble, Div. of Owens-Illinois Inc., Toledo, OH) with polypropylene or Teflon® cap liners. If possible, submit bulk or wipe samples in these vials. Tin or other metal cap liners should not be used because the metal and azide may react.

2.4. Sampling Procedure - Air Samples

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Very few industrial operations are conducted where $HN_3$ exists and $NaN_3$ does not. The tube is used to capture the $HN_3$ while the filter will capture $NaN_3$. Particulate $NaN_3$ can be captured in the glass wool plug of the tube; however, a pre-filter is more effective in capturing the particulate.

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2.4.1. Connect the cassette/tube assembly to the calibrated sampling pump. Ensure that sampled air will enter the tube following the direction of the arrow sign (--->) stamped on the outer glass. Place the sampling device on the employee such that air is sampled from the breathing zone.

2.4.2. Use a flow rate of 1 L/min and a minimum sampling time of 5 min. Take additional samples as necessary.

2.4.3. After sampling, place plastic end caps tightly on both ends of the tube and the filter cassette. Apply OSHA Form 21 seals. Record the sampling conditions such as sampling time, air volume, etc. on the OSHA 91A form. When other compounds are known or suspected to be present in the air, record such information and transmit with the samples. See note in Section 2.7., regarding sample shipment.

2.4.4. Use the same lot of ISG tubes and PVC filters for blank and collected samples. Prepare and handle the blank sorbent tube(s) and filter cassette(s) in exactly the same manner as the sample tubes except that no air is drawn through blanks.

2.5. Sampling Procedure - Wipe Samples for Sodium Azide Particulate

A skin designation has been assigned by OSHA to these azide-containing compounds.

2.5.1. Wear clean, impervious, disposable glove when taking each wipe sample.

2.5.2. *DO NOT* moisten the wipe PVC or glass fiber filters with deionized water prior to use. *Use a dry filter* to wipe for surface contamination of azide compounds.

2.5.3. If possible, wipe a surface area covering 100 $cm^2$.

2.5.4. Fold the wipe filter sample with exposed side in. See note in Section 2.7., regarding sample shipment.

2.5.5. Transfer the wipe sample into a 20-mL scintillation vial and seal with vinyl tape. Securely wrap an OSHA-21 seal length-wise from vial top to bottom.

2.5.6. Prepare a blank wipe sample by placing an unused wipe filter sample in a scintillation vial. Seal the vial as discussed in Section 2.5.5.

2.6. Sampling Procedure - Bulk Samples

2.6.1. Take a representative sample of the bulk material in the workplace. Transfer the bulk material into a 20-mL scintillation vial and seal with vinyl or electrical tape. Securely wrap an OSHA-21 seal length-wise from vial top to bottom.

2.6.2. The type of bulk sample should be stated on the OSHA 91A and cross-referenced to the appropriate air sample(s).

2.7. Shipment

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Note: If a delay in shipment is anticipated (> 2 days after taking samples), remove the PVC filters from the cassettes and place in individual scintillation vials. Add 5.0 mL of desorbing solution (Section 2.1.6.) to each scintillation vial containing a PVC filter. Add 10 mL of desorbing solution to each scintillation vial containing a wipe filter sample. Refrigerate any tube samples until shipment.

2.7.1. Submit at least one blank sample with each set of air or wipe samples.

2.7.2. Send the samples to the laboratory *as soon as possible* with the OSHA 91A paperwork requesting total azide analysis.

2.7.3. Bulk samples should be shipped separately from air samples. They should be accompanied by Material Safety Data Sheets if possible. Check current shipping restrictions and ship to the laboratory by the appropriate method.

## 3. Analysis

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Note: Upon receipt by the laboratory, all samples are stored under refrigeration (~4°C) until analysis. This includes wipe, filter, sorbent, and bulk samples. Samples inadvertently stored at room temperature need to be analyzed within 10 days.

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3.1. Safety Precautions

3.1.1. Refer to appropriate IC instrument manuals and the Standard Operating Procedure (SOP) for proper instrument operation (5.14.).

3.1.2. Observe laboratory safety regulations and practices.

3.1.3. Sodium azide is highly toxic and presents a severe explosion hazard if shocked or heated. Use appropriate personal protective equipment such as safety glasses, goggles, gloves, and lab coat when handling this chemical. Prepare solutions in an exhaust hood. Store unused solutions in a refrigerator or dispose of properly.

3.2. Equipment

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Chromatographic equipment which allows for analyte contact with metal surfaces MAY reduce the amount of azide present. It is recommended to use equipment in which samples have minimal or no contact with metal surfaces. Analysts should avoid using metal spatulas when weighing azide compounds, or IC pre-column or columns contaminated with heavy metals.

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3.2.1. Ion chromatograph (Model 4000i or 4500i Dionex, Sunnyvale, CA) equipped with a variable UV detector.

3.2.2. Automatic sampler (Dionex Model AS-1) and sample vials (0.5 mL).

3.2.3. Laboratory automation system: Ion chromatograph interfaced to a data reduction system (AutoIon 450, Dionex).

3.2.4. Separator and guard columns, anion (Model HPIC-AS9 and AG9, Dionex).

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Note: The pH of the eluant must be maintained between 2-11 and hydroxide ion must *not* be present in significant amounts if Dionex AS9 and AG9 columns are used. Irreversible damage to the columns (guard and separator column) will result.

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3.2.5. Disposable syringes (1 mL).

3.2.6. Plastic or Teflon®-coated spatulas used for weighing $NaN_3$.

3.2.7. Miscellaneous volumetric glassware: Micropipettes, 10-mL volumetric flasks, 25-mL Erlenmeyer flasks, graduated cylinders, and beakers.

3.2.8. Scintillation vials, glass, 20-mL, with polypropylene- or Teflon®-lined caps.

3.2.9. Equipment for eluant degassing (vacuum pump, ultrasonic bath).

3.2.10. Analytical balance (0.01 mg).

3.2.11. Exhaust hood.

3.3. Reagents - All chemicals should be at least reagent grade.

3.3.1. Principal reagents:

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**CAUTION:** $NaN_3$ can be a dangerous chemical, and can cause an explosion when shocked or heated. It is also a skin irritant and a hypotensive agent. Avoid skin contact and handle this chemical and any solutions with care. Do not dry $NaN_3$ in a drying oven!

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Sodium carbonate ($Na_2CO_3$)
Sodium bicarbonate ($NaHCO_3$)

Sodium azide ($NaN_3$)
Hydrochloric acid (HCl)
Deionized water (DI $H_2O$) - specific conductance <10 $\mu$S.

3.3.2. Eluent and desorbing solution (0.9 mM $Na_2CO_3$ + 0.9 mM $NaHCO_3$):

Dissolve 0.191 g $Na_2CO_3$ and 0.151 g $NaHCO_3$ in 2.0 L DI $H_2O$. Sonicate this solution and degas under vacuum for 15 min. Prepare weekly.

3.3.3. Azide ($N_3^-$) stock standard (1,000 $\mu$g/mL):

Prepare the azide stock standard in an exhaust hood. Carefully weigh 1.5476 g of $NaN_3$ (Aldrich Chemical Company, Inc., Milwaukee, WI). Dissolve and dilute to 1.0 L with DI $H_2O$. Prepare monthly.

3.3.4. Azide ($N_3^-$) standard solutions (100, 10, and 1 $\mu$g/mL):

Perform serial dilutions of the 1,000 $\mu$g/mL $N_3^-$ stock standard using volumetric pipets and flasks. Dilute to the mark with eluant. Prepare every two weeks. The larger standards (100 and 10 $\mu$g/mL) can be used as working standards, if necessary.

3.3.5. Dispose of azide or azide solutions according to the chemical manufacturer, and local or federal waste disposal guidelines. A method for disposal of aqueous azide solutions recommended by the Royal Society of Chemistry (5.15.) is to dilute the solution greatly with water and then run to waste.

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**CAUTION:** Do not dispose of untreated azides or concentrated azide solutions by pouring down sink drains.

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3.4. Working Standard Preparation

3.4.1. Prepare $N_3^-$ working standards in the ranges specified below:

| Working Std ($\mu$g/mL) | Std Solution ($\mu$g/mL) | Aliquot (mL) | Eluant Added (mL) |
|---|---|---|---|

| | | | |
|---|---|---|---|
| 0.05 | 1.0 | 0.5 | 9.5 |
| 0.10 | 1.0 | 1.0 | 9.0 |
| 0.20 | 1.0 | 2.0 | 8.0 |
| 0.50 | 1.0 | 5.0 | 5.0 |
| 0.75 | 1.0 | 7.5 | 2.5 |
| 1.00 | 1.0 | * | * |

* Already prepared in Section 3.3.4.

3.4.2. To prepare 10 mL of each working standard, pipette an appropriate aliquot (Aliquot column listed above) of the 1.0 µg/mL standard solution into a scintillation vial or Erlenmeyer flask. Add the specified amount of eluant (Eluant Added column). As an alternative, pipet each aliquot into a 10-mL volumetric flask and dilute to volume with eluant.

3.5. Sample Preparation - Air Samples

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Note: Samples desorbed in the field (Section 2.7.) are ready for analysis (Section 3.7.).

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3.5.1. Remove filter cassette and tube samples from the refrigerator and allow them to warm to room temperature.

3.5.2. *Tube Samples:*

Carefully remove the end glass wool plug. The sorbent should always be removed from the glass tube via the opposite end of collection (i.e. backup section is removed first). This will minimize the possibility of contamination from any collected particulate.

3.5.3. Transfer each section of the ISG and glass wool plugs and place in separate 25-mL Erlenmeyer flasks or 20-mL scintillation vials. Place the front glass wool plug and front ISG section (150 mg) in one container and place the middle and end glass wool plug in another container with the backup ISG section (75 mg).

3.5.4. Pipette 3.0 mL of desorbing solution into each container. Cap each flask tightly and allow the solution to sit for at least 60 min. Swirl the solution occasionally.

3.5.5. *Filter Samples:*

Carefully remove each filter from the cassette and place into individual 20-mL scintillation vials. Add 5.0 mL of desorbing solution to each vial. Cap each vial tightly and allow the solution to sit for at least 60 min. Swirl the solution occasionally.

3.6. Sample Preparation - Wipe and Bulk Samples

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Note: Samples desorbed in the field (Section 2.7.) are ready for analysis (Section 3.7.).

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3.6.1. Remove wipe and bulk samples from the refrigerator and allow them to warm to room temperature.

3.6.2. Weigh out representational aliquots of bulks.

3.6.3. Carefully transfer wipe samples, and previously weighed aliquots of bulk samples to separate labeled 20-mL scintillation vials and add 10.0 mL of desorbing solution into each vial. Cap each vial tightly and allow the solution to sit for at least 60 min. Swirl the solution occasionally.

3.7. Sample Analysis

3.7.1. Pipette a 0.5- to 0.6-mL portion of each standard or sample solution into separate automatic sampler vials. Place a filtercap into each vial. The large filter portion of the cap should face the solution.

3.7.2. Load the automatic sampler with labeled samples, standards, and blanks.

3.7.3. Set up the ion chromatograph in accordance with the SOP (5.14.)

Typical operating conditions for a Dionex 4500i with a variable wavelength UV detector and an automated sampler are listed below:

*Ion Chromatograph*

| | |
|---|---|
| Eluant: | 0.9 mM $Na_2CO_3$/0.9 mM $NaHCO_3$ |
| Column temperature: | ambient |
| Anion pre-column: | AG9 |
| Anion separator column: | AS9 |
| Variable UV wave length: | 210 nm |
| Variable UV output range: | 0.01 AU |
| Sample injection loop: | 50 $\mu$L |

*Pump*

| | |
|---|---|
| Pump pressure: | ≈500 psi |
| Flow rate: | 1 mL/min |

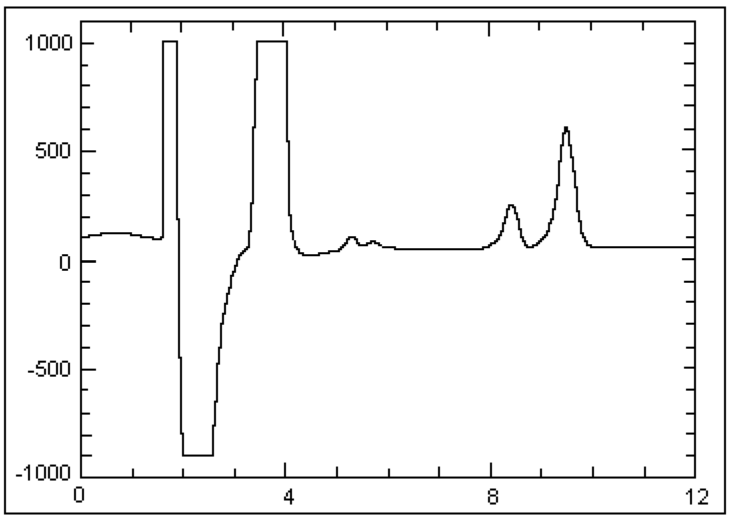
*Chromatogram*

| | |
|---|---|
| Run time: | 12 min |
| Peak retention time: | 8 to 9 min for $N_3^-$ |

3.7.4. Follow the SOP for further instructions regarding analysis (5.14.).

3.8. Calculations

3.8.1. After the analysis is completed, retrieve the peak areas or heights for the azide anion. Obtain hard copies of chromatograms from a printer. An example chromatogram of a solid sorbent sample collected at an hydrozoic acid concentration of approximately 2 × PEL is shown below:




**Example chromatogram of a solid sorbent sample collected at an hydrozoic acid concentration of approximately 2 × PEL**

| Sample Name: AZS-124 | | Detector: VDM-1 | | | | | |
|---|---|---|---|---|---|---|---|
| REPORT | VOLUME | DILUTION | POINTS | RATE | START | STOP | AREA REJECT |
| External | 1 | 1 | 3605 | 5Hz | 0.00 | 12.02 | 100000 |

| Peak No. | Retention Time (Min) | Component Name | --------Peak--------- | |
|---|---|---|---|---|
| 1 | 0.77 | | 28,132 | 1,527,608 |
| 2 | 1.67 | | 1,193,355 | 26,810,606 |
| 3 | 3.48 | | 612,318 | 19,049,090 |
| 4 | 5.28 | | 53,446 | 791,025 |
| 5 | 5.72 | | 20,583 | 286,812 |
| 6 | 8.42 | Azide | 196,012 | 4,072,104 |
| 7 | 9.50 | Nitrate | 550,223 | 12,829,040 |

3.8.2. Prepare a concentration-response curve by plotting the peak areas or peak heights versus the concentration of the $N_3^-$ standards in $\mu$g/mL.

3.8.3. Calculate the air concentration of $NaN_3$ (in mg/m$^3$) for each filter or sorbent sample:

$$W_{SA} = (\mu g/mL\ N_3^-)(SV)(GF)_{SA}$$

$$mg/m^3\ NaN_3 = \frac{W_{SA} - W_B}{AV}$$

Where:

| | | |
|---|---|---|
| $W_{SA}$ | = | Total $\mu$g of $NaN_3$ in the sample$W_B$ = Total $\mu$g of $NaN_3$ in the blank sample |
| $\mu g/mL\ N_3^-$ | = | Amount found (from curve) |
| SV | = | Solution volume (mL) from Section 3.5.3. |
| $(GF)_{SA}$, $NaN_3/N_3^-$ | = | Gravimetric factor = 1.5476 |

AV = Air volume (L)

3.8.4. Calculate the total concentration of $NaN_3$ (in $\mu$g) in each wipe or bulk sample using the appropriate equation:

$$\mu g\ NaN_3 = W_{SA} - W_B \qquad \text{(Wipe Samples)}$$

$$NaN_3\ \%\ (w/w) = \frac{W_{SA} \times 100\%}{S \times F} \qquad \text{(Bulk Samples)}$$

Where:

S = Sample wt, mg = Aliquot of bulk taken in Section 3.6.2.
F = 1,000 $\mu$g/mg

3.9. Reporting Results

3.9.1. Add the PVC filter and sorbent results together for each sample. Report this sum result to the industrial hygienist as mg/m$^3$ $NaN_3$ (total).

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Note: Vapor phase and particulate results should be combined to determine compliance and to minimize confusion. Although the vapor phase is a ppm value, the OSHA regulation stipulates "sodium azide" as sodium azide or as hydrozoic acid (5.13.). The total exposure to both phases needs to be considered for compliance and the results need to be reported as either total mg/m$^3$ $NaN_3$ or total ppm $HN_3$ to minimize confusion. If it is necessary to determine the ppm amount of $HN_3$, see the Appendix.

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3.9.2. Wipe sample concentrations are reported as total micrograms or milligrams of $NaN_3$.

3.9.3. Bulk sample results are reported as approximate percent by weight sodium azide. Due to differences in sample matrices between bulks and analytical standards, bulk results are approximate.

## 4. Backup Data

This method has been validated for a 5-L, 5-min sample taken at a flow rate of 1 L/min. The method validation was conducted near the OSHA Ceiling PEL. The sampling media used during the validation consisted of two-section tubes packed with 150-mg of ISG for the front and also 150 mg for the backup sections. Tubes were obtained commercially from SKC (Lot no. 782, Cat. no. 226-55, SKC Inc., Eighty Four, PA).

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Note: After the validation was completed, the manufacturer reduced the amount of sorbent in the backup section to 75 mg, and reduced the length of the sampling tube from 110 mm to 70 mm. This change produces a smaller, more convenient sampling train (pre-filter cassette/sampling tube) and should not affect results.

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The validation consisted of the following experiments and discussion:

1. An analysis of 24 spiked samples was performed (8 samples each at 2 ×, 1 ×, and 0.5 × the Ceiling PEL) to evaluate desorption efficiency (DE).
2. A sampling and analysis of 18 samples (6 samples each at 2 ×, 1 ×, and 0.5 × Ceiling PEL) collected from dynamically generated test atmospheres at 50% RH. to determine bias and overall error.
3. A determination of the sampling media collection efficiency at approximately 0.26 ppm (≈2 × Ceiling PEL).
4. A determination of potential breakthrough.
5. An evaluation of storage stability at room (20 to 25°C), refrigerator (0 to 4°C), and freezer (-10 to -14°C) temperatures for 64 collected samples.
6. A determination of any significant effects on results when sampling at different humidities.
7. A determination of the qualitative and quantitative detection limits.
8. Evaluation of a pre-filter/cassette assembly or foam for use during sampling.
9. Determination of stability of $NaN_3$ on wipe sampling media.
10. Summary.

A generation system was assembled, as shown in Figure 1, and used for all experiments except detection limit determinations. All samples were analyzed by IC. All known concentrations of generated test atmospheres were calculated from impinger samples which contained 1.0 mM $Na_2CO_3$/1.0 mM $NaHCO_3$ solutions. These impinger samples were taken side-by-side with any ISG samples.

All results were calculated from concentration-response curves and statistically examined for outliers. In addition, the analysis (Section 4.1.) and sampling and analysis results (Section 4.2.) were tested for homogeneity of variance. Possible outliers were determined using the Treatment of Outliers test (5.16.). Homogeneity of variance was determined using Bartlett's test (5.17.). Statistical evaluation was conducted according to the Inorganic Methods Evaluation Protocol (5.18.). The overall error (OE) (5.18.) was calculated using the equation:

$$OE_i\% = \pm(|bias_i| + 2CV_i) \times 100\% \text{ (95\% confidence level)}$$

Where *i* is the respective sample pool being examined.

4.1. Analysis

Twenty-four samples were prepared by adding known amounts of $NaN_3$ (as $N_3^-$) stock solution to the ISG tubes to determine desorption efficiencies (DEs) for the analytical portion of the method.

4.1.1. *Procedure:* Sampling tubes containing ISG were spiked using a 25-µL syringe (Hamilton Microliter ®/Gastight® Syringe, Hamilton Co., Reno, NV). Spikes were 0.5, 1.0, and 2.0 µg $N_3^-$. These levels correspond approximately to 0.5, 1, and 2 times the Ceiling PEL for a 5-L air sample at a 1-L/min flow rate.

4.2. Sampling and Analysis

To determine the precision and accuracy of the method, known concentrations of $HN_3$ were generated, samples were collected and then analyzed. A block diagram of the generation system used is shown in Figure 1.

4.2.1. *Procedure:*

1. Test atmospheres of $HN_3$ were generated using a syringe pump (Model 355 syringe pump, Sage Instruments, Cambridge, MA) and a dynamic generation system. To prepare the atmospheric concentrations, a 1,000 µg/mL azide solution (prepared from $NaN_3$, EM Science, Cherry Hill, NJ) was used. For each $HN_3$ atmosphere generated, 100 µL of concentrated HCl was added to 10 mL of the azide solution to drive the reaction of $NaN_3$ to $HN_3$. The $HCl/NaN_3/H_2O$ solution was immediately loaded into a 10-mL disposable syringe driven between 0.13 and 0.52 mL/h through 60 cm of a Teflon® needle (KF30TF needle, Hamilton Co., Reno, NV) into a glass mixing chamber. The mixing chamber was connected to a filtered and humidified airstream.

2. Dynamic generation system
   A Miller-Nelson Research Inc. flow, temperature, and humidity control system (Model HCS-301, Monterey, CA) was used to control and condition the airstream. All generation system fittings and connections were Teflon®. The $HN_3$ concentrations were varied by either adjusting the dilution airstream volume or the speed of the syringe pump delivering the azide. The dilution airstream was adjusted using the mass flow controller of the Miller-Nelson system. The system was set to generate test atmospheres at 50% RH and 25°C.

3. The total flow rate of the generation system was measured using a dry test meter.

4. Side-by-side solid-sorbent and impinger samples were taken from the sampling manifold using constant-flow pumps. Alpha 1 pumps (E.I. Du Pont de Nemours & Co.,

Wilmington, DE) and Gilian® Gil-Air SC pumps (Gilian Instrument Corp., W. Caldwell, NJ) were used for impinger and ISG samples, respectively. For the ISG samples, pump flow rates were approximately 1 L/min and sampling time was 5 min. For impinger samples, a 1 L/min sampling rate for 15 min was used. Generation system concentrations were approximately 0.5, 1, and 2 times the OSHA Ceiling PEL.

4.2.2. An independent source was used for $NaN_3$ analytical standard preparations (Aldrich Chemical Company, Inc., Milwaukee, WI). All samples and standards were analyzed in accordance with Section 3 of this method.

4.2.3. *Results:* The results are shown in Table 2) and spiked sample (Table 1) results each passed the Bartlett's test and were pooled to determine a total CV ($CV_T$) for the sampling and analytical method. For the experiments, the pooled coefficients of variation, bias, and OE are as follows:

| | | |
|---|---|---|
| $CV_1$ (pooled) = 0.023; | $CV_2$ (pooled) = 0.051 | |
| $CV_T$ (pooled) = 0.052; | bias = -0.022; | OE = ±12.6% |

4.3. Collection Efficiency

*Procedure:* Six commercially-prepared sampling tubes were used for collection at a concentration of approximate times the OSHA Ceiling PEL for 5 min at 1 L/min (50% RH and 25°C). The amounts of $HN_3$ vapor collected in the section (150 mg of sorbent) and second section (150 mg) were determined. The collection efficiency (CE) was calculated by dividing the amount of $HN_3$ collected in the first section by the total amount of $HN_3$ collected in the and second sections.

*Results:* The results in Table 3 show a CE of 100%. No $HN_3$ was found in the second sorbent section for the CE experiment.

4.4. Breakthrough

(Note: Breakthrough is defined as >5% loss of analyte through the sampling media at 50% RH)

*Procedure:* The same procedure as the CE experiment (Section 4.3.) was used with two exceptions: The generati concentration was increased to a level approximately 9 times the Ceiling PEL, and samples were taken at 1 L/mir 30 min.

The amount of breakthrough for each sampling tube was calculated by dividing the amount collected in the secor section by the total amount of $HN_3$ collected in the first and second sections.

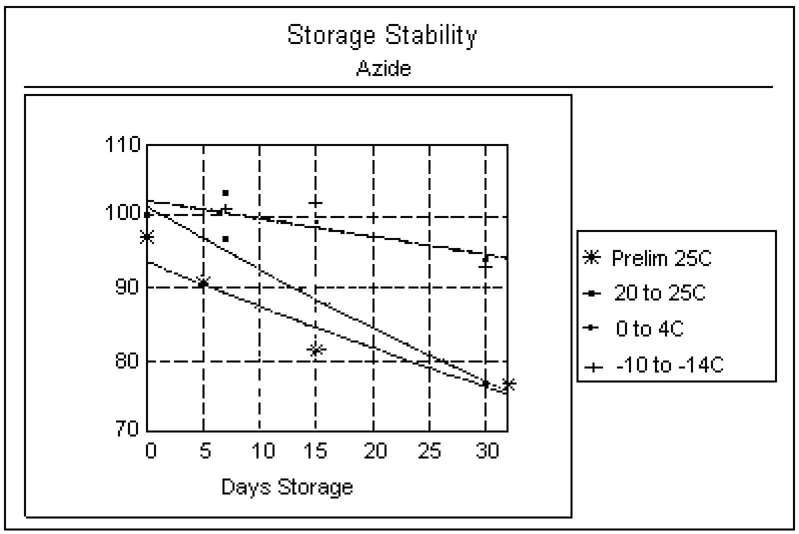
*Results:* No breakthrough of $HN_3$ into the second section was found. Results are shown in Table 4.

4.5. Storage Stability

*Procedure:* Two tests were conducted to assess storage stability. The first was a preliminary study of storage at room temperature (20 to 25°C) after $HN_3$ collection. Twenty-four samples were taken near the OSHA Ceiling PEL of 0.1 ppm. After collection, all samples were stored under normal laboratory conditions (20 to 25°C) on a lab bench and were not protected from light. Six samples were initially desorbed and analyzed, then six samples were desorbed and analyzed after various periods of storage (5, 15, and 32 days).

An additional test was conducted by generating 40 samples (4 room-temperature samples at day 15 were discarded due to analytical problems) for a temperature-dependent storage stability test, including 4 control samples (used for day 0). The samples were separated into 3 groups and each group consisted of 4 samples per storage period. A group was stored at either room, refrigerated, or freezer temperature. The same analytical procedure as the previous storage test was used. Samples were analyzed after 0, 7, 15, and 30 days.

*Results:* As shown in Table 5a and the graph below, the results of the first test show the mean of samples analyzed after 32 days was only 77% of the value of day 0. Table 5b and the graph below show the results of the second study at different temperatures. The recovery is only 77% of the value of day 0 after a 30-day storage at room temperature. This drastic change was not noted for samples stored at refrigerated or freezer temperatures; however, a slight decrease in sample recoveries (93 - 94%) after 30 days was apparent.




**Storage Stability Results**

4.6. Humidity Study

*Procedure:* A study was conducted to determine any effect on results when samples are collected at different humidities. Samples were taken using the generation system and procedure described in Section 4.2. Test atmospheres were generated at 25°C and at approximately 0.5, 1, and 2 times the OSHA Ceiling PEL. Relative humidities of 30%, 50%, and 80% were used at each concentration level tested.

*Results:* Results of the humidity tests are listed in Table 6. An F test was used to determine if any significant effect occurred when sampling at different humidities. As shown, the calculated F values are less than critical F values (5.19.) for all the concentrations tested and no significant difference in results occurred across the humidity ranges tested.

4.7. Qualitative and Quantitative Detection Limit Study

*Procedure:* Low concentration samples were prepared by spiking desorbing solutions (Section 3.3.2.) with aliquots of aqueous standards prepared from $NaN_3$ (Section 3.3.4.). These samples were analyzed using a 50-$\mu$L sample injection loop and a variable wavelength UV detector setting of 0.01 absorbance unit (AU). A derivation of the International Union of Pure and Applied Chemistry (IUPAC) detection limit equation (5.20.) was used to calculate detection limits.

4.8. Pre-filter Evaluation

*Procedure:* Past research regarding aerosols (5.21.) has indicated that particulate in the air sampled may penetrate any glass wool plugs and the sorbent when using conventional sampling tubes. A pre-filter can be used to assist in capturing particulate before entry into the sampling tube. A study was conducted to evaluate the possibility of $HN_3$ reacting with a pre-filter/cassette or foam sampling device to capture $NaN_3$ or other particulate. Evaluations were performed using either ISG sampling tubes with pre-filter sampling assemblies (PVC filter/spacer support/cassette), or with polyurethane foam [foam used in the combination sampling device for $SO_2$ (Type II tube), OSHA Method No. ID-200] for particulate collection.

A test was conducted by taking four ISG samples without pre-filters side-by-side with four ISG samples connected with pre-filters. This test was repeated with foam plugs instead of the pre-filters. Samples were taken such that the test atmosphere entered the pre-filter or foam first and then entered the ISG. Short pieces of Tygon® tubing were used to connect the cassettes and ISG sampling tubes. All samples were taken at a flow rate of about 0.8 L/min for 5 min. The generation system concentration was approximately 1.5 times the Ceiling PEL.

**Results:** The results of the comparison of ISG samples taken, with and without pre-filter or foam, are shown in Tables 8a and 8b, respectively. As shown, a difference in the amount of $HN_3$ collected was not noted between the pre-filter/ISG and ISG, or foam/ISG. The PVC pre-filter/cassette or the foam does not appear to inhibit the collection of $HN_3$ when using the sampling conditions stated in Section 2. The PVC filter/cassette assembly is recommended for particulate sample collection. The foam may be validated for use in the future to develop a combination sampling device for collection of both $NaN_3$ and $HN_3$. The ability of the foam to effectively capture $NaN_3$ needs to be further examined.

4.9. Stability of $NaN_3$ on Wipe Sampling Media

*Procedure:* A determination of the stability of $NaN_3$ was conducted using 37-mm glass fiber filters (Cat. no. 61715, Gelman Instrument Company, Ann Arbor, MI) and smear tabs (Lot. no. 3034, Whatman LabSales Inc., Hillsboro, OR). The stability of sodium azide on PVC membranes has been previously reported as stable up to 10 days of storage (5.6.). Glass fiber filters or smear tabs were spiked using a 25-µL syringe (Hamilton Microliter®/Gastight® Syringe, Hamilton Co., Reno, NV). Solution spikes contained between 7 and 15 µg $NaN_3$. Filters were allowed to dry and were stored for 3 days on a lab bench, then refrigerated until analysis.

*Results:* The precision and accuracy results for glass fiber filters and smear tabs are shown below (F/T = Found/Theoretical recovery):

| Collection Media | N | Mean (F/T) | Std Dev | CV |
|---|---|---|---|---|
| Glass Fiber Filters | 5 | 1.001 | 0.036 | 0.036 |
| Smear Tabs | 5 | 0.412 | 0.134 | 0.325 |

The recovery data shows that azide is unstable on cellulose media and stable on glass fiber filters.

4.10. Summary

The validation results indicate the method meets both the NIOSH and OSHA criteria for accuracy and precision (5.17., 5.18.). Performance during collection efficiency, breakthrough, and humidity tests is adequate. Although it appears that the recovery dramatically decreases when storing collected samples at room temperature after 15 days, no losses were found when storing the sampling tubes after sample collection in a refrigerator or freezer. It is recommended to analyze samples within 10 days if samples are stored without refrigeration and within 30 days if refrigeration is used. Detection limits are adequate when samples are taken for 5 min at 1 L/min. The method is adequate for monitoring occupational exposures to the OSHA Ceiling PEL.

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Table 1
Azide (as $N_3^-$) Analysis - Desorption Efficiency (DE)

(OSHA-PEL)

| Taken ($\mu$g $N_3^-$) | Found ($\mu$g $N_3^-$) | DE (F/T) | N | Mean | Std Dev | CV |
|---|---|---|---|---|---|---|
| (0.5 × PEL) | | | | | | |
| 0.500 | 0.500 | 1.000 | | | | |
| 0.500 | 0.515 | 1.030 | | | | |
| 0.500 | 0.520 | 1.040 | | | | |
| 0.500 | 0.500 | 1.000 | | | | |
| 0.500 | 0.505 | 1.010 | | | | |
| 0.500 | 0.510 | 1.020 | | | | |
| 0.500 | 0.465 | 0.930 | | | | |
| 0.500 | 0.525 | 1.050 | | | | |
| | | | 8 | 1.010 | 0.037 | 0.037 |
| (1 × PEL) | | | | | | |
| 1.000 | 0.995 | 0.995 | | | | |
| 1.000 | 0.985 | 0.985 | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| 1.000 | 0.995 | 0.995 | | | | |
| 1.000 | 1.000 | 1.000 | | | | |
| 1.000 | 1.015 | 1.015 | | | | |
| 1.000 | 0.995 | 0.995 | | | | |
| 1.000 | 0.995 | 0.995 | | | | |
| 1.000 | 1.000 | 1.000 | | | | |
| | | | 8 | 0.998 | 0.008 | 0.008 |
| (2 × PEL) | | | | | | |
| 2.000 | 1.980 | 0.990 | | | | |
| 2.000 | 1.960 | 0.980 | | | | |
| 2.000 | 2.000 | 1.000 | | | | |
| 2.000 | 1.990 | 0.995 | | | | |
| 2.000 | 1.975 | 0.988 | | | | |
| 2.000 | 2.010 | 1.005 | | | | |
| 2.000 | 2.035 | 1.018 | | | | |
| 2.000 | 1.970 | 0.985 | | | | |
| | | | 8 | 0.995 | 0.012 | 0.012 |

F/T = Found/Taken DE = Desorption Efficiency

$CV_1$ (Pooled) = 0.023 Average DE = 1.001

The average DE is very close to 1.0; therefore, a DE correction is not necessary.

Table 2
Hydrazoic Acid Sampling and Analysis - Ceiling PEL Determination *
(25°C and 50% RH)

(OSHA-PEL)

| Taken (ppm $HN_3$) | Found (ppm $HN_3$) | Recovery (F/T) | N | Mean | Std Dev | CV | OE (±%) |
|---|---|---|---|---|---|---|---|

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| (0.5 × PEL) | | | | | | | |
| 0.057 | 0.053 | 0.930 | | | | | |
| 0.057 | 0.058 | 1.018 | | | | | |
| 0.057 | 0.053 | 0.930 | | | | | |
| 0.057 | 0.061 | 1.070 | | | | | |
| 0.057 | 0.056 | 0.982 | | | | | |
| 0.057 | 0.054 | 0.947 | | | | | |
| | | | 6 | 0.980 | 0.056 | 0.057 | 13.4 |
| (1 × PEL) | | | | | | | |
| 1.130 | 0.129 | 0.992 | | | | | |
| 1.130 | 0.121 | 0.931 | | | | | |
| 1.130 | 0.135 | 1.038 | | | | | |
| 1.130 | 0.117 | 0.900 | | | | | |
| 1.130 | 0.122 | 0.938 | | | | | |
| 1.130 | 0.121 | 0.931 | | | | | |
| | | | 6 | 0.955 | 0.050 | 0.053 | 15.1 |
| (2 × PEL) | | | | | | | |
| 0.263 | 0.259 | 0.985 | | | | | |
| 0.263 | 0.267 | 1.015 | | | | | |
| 0.263 | 0.252 | 0.958 | | | | | |
| 0.263 | 0.251 | 0.954 | | | | | |
| 0.263 | 0.276 | 1.049 | | | | | |
| 0.263 | 0.272 | 1.034 | | | | | |
| | | | 6 | 0.999 | 0.040 | 0.040 | 8.01 |

F/T = Found/Taken
Bias = -0.022
$CV_2$ (Pooled) = 0.051
$CV_T$ (Pooled) = 0.052
Overall Error (Total) = ±12.6%

*Samples were taken for 5 min.

Table 3
Collection Efficiency
(2 × PEL, 25°C & 50% RH)

| | ------------------ppm $HN_3$ ------------------- | | |
|---|---|---|---|
| Sample No. | First Section | Second Section | % Collection Efficiency |
| 1 | 0.259 | ND | 100.0 |
| 2 | 0.267 | ND | 100.0 |
| 3 | 0.252 | ND | 100.0 |
| 4 | 0.251 | ND | 100.0 |
| 5 | 0.273 | ND | 100.0 |
| 6 | 0.273 | ND | 100.0 |

Notes:
a. Sampled at 1 L/min for 5 min.
b. Samples desorbed using a sample solution volume of 3.0 mL
c. ND = None detectable (<0.001 ppm $HN_3$)

Table 4
Breakthrough Study
(25°C and 50% RH)

| | ------------------ppm $HN_3$ ------------------- | | |
|---|---|---|---|
| Sample No. | First Section | Second Section | % Breakthrough |
| 1 | 0.933 | ND | |
| 2 | 0.940 | ND | 0 |
| 3 | 0.897 | ND | 0 |
| 4 | 0.889 | ND | 0 |
| 5 | 0.938 | ND | 0 |
| 6 | 0.891 | ND | 0 |

| | | | |
|---|---|---|---|
| 7 | 0.913 | ND | 0 |
| 8 | 0.925 | ND | 0 |

Notes:
a. Sampled at 1 L/min for 30 min
b. Due to the large concentration generated and the analytical sensitivity, the front ISE sections of sampling tubes were desorbed using larger sample solution volumes of 10.0 mL.
c. ND = None detectable (<0.001 ppm $HN_3$)

Table 5a
Preliminary Test
Storage Stability - $HN_3$
(1 × PEL, 25°C, and 50% RH)

| Day | Air Vol (L) | Found (--ppm $HN_3$--) | Taken | N | Mean | Std Dev | CV | Recovery (%) |
|---|---|---|---|---|---|---|---|---|
| 0 | 4.21 | 0.129 | 0.130 | | | | | |
| | 4.21 | 0.121 | 0.130 | | | | | |
| | 4.21 | 0.135 | 0.130 | | | | | |
| | 4.21 | 0.117 | 0.130 | | | | | |
| | 4.21 | 0.122 | 0.130 | | | | | |
| | 4.21 | 0.121 | 0.130 | | | | | |
| | | | | 6 | 0.124 | 0.007 | 0.053 | 95.4 |
| 5 | 4.21 | 0.116 | 0.130 | | | | | |
| | 4.21 | 0.124 | 0.130 | | | | | |
| | 4.21 | 0.116 | 0.130 | | | | | |
| | 4.21 | 0.121 | 0.130 | | | | | |
| | 4.21 | 0.117 | 0.130 | | | | | |
| | 4.21 | 0.114 | 0.130 | | | | | |
| | | | | 6 | 0.118 | 0.004 | 0.032 | 90.8 |
| 15 | 3.92 | 0.106 | 0.130 | | | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 3.92 | 0.106 | 0.130 | | | | | |
| | 3.92 | 0.107 | 0.130 | | | | | |
| | 3.92 | 0.113 | 0.130 | | | | | |
| | 3.92 | 0.101 | 0.130 | | | | | |
| | 3.92 | 0.101 | 0.130 | | | | | |
| | | | | 6 | 0.106 | 0.004 | 0.042 | 81.3 |
| 32 | 4.21 | 0.096 | 0.130 | | | | | |
| | 4.21 | 0.099 | 0.130 | | | | | |
| | 4.21 | 0.104 | 0.130 | | | | | |
| | 4.21 | 0.100 | 0.130 | | | | | |
| | 4.21 | 0.108 | 0.130 | | | | | |
| | 4.21 | 0.092 | 0.130 | | | | | |
| | | | | 6 | 0.100 | 0.006 | 0.057 | 76.8 |

Table 5b
Storage Stability - $HN_3$
at
Room, Refrigerated and Freezer Temperatures
(Known $HN_3$ Concentration = 0.108 ppm at 50% RH)

| Temperature: | Room | | | Refrigerated | | Freezer | |
|---|---|---|---|---|---|---|---|
| Day | Air Vol (L) | | Found (ppm) | Air Vol (L) | Found (ppm) | Air Vol (L) | Found (ppm) |
| 0 | 3.05 | | 0.116 | * | * | * | * |
| | 3.05 | | 0.120 | * | * | * | * |
| | 3.05 | | 0.097 | * | * | * | * |
| | 3.05 | | 0.099 | * | * | * | * |
| | N | = | 4 | | * | | * |
| | Mean | = | 0.108 | | * | | * |
| | Std Dev | = | 0.012 | | * | | * |
| | | = | 0.108 | | * | | * |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $CV_2$ | = | 100% | | | | | |
| | Recovery | | | | | | | |
| 7 | 3.54 | | 0.121 | 3.05 | 0.098 | 3.54 | 0.127 |
| | 3.54 | | 0.115 | 3.05 | 0.126 | 3.54 | 0.108 |
| | 3.54 | | 0.095 | 3.05 | 0.105 | 3.54 | 0.098 |
| | 3.54 | | 0.087 | 3.05 | 0.116 | 3.54 | 0.104 |
| | N | = | 4 | | 4 | | 4 |
| | Mean | = | 0.105 | | 0.111 | | 0.109 |
| | Std Dev | = | 0.016 | | 0.012 | | 0.013 |
| | $CV_2$ | = | 0.154 | | 0.111 | | 0.115 |
| | Recovery | = | 96.8% | | 103% | | 101% |
| 15 | + | | + | 3.54 | 0.120 | 3.05 | 0.129 |
| | + | | + | 3.54 | 0.102 | 3.05 | 0.101 |
| | + | | + | 3.54 | 0.100 | 3.05 | 0.102 |
| | + | | + | 3.54 | 0.106 | 3.05 | 0.110 |
| | N | = | + | | 4 | | 4 |
| | Mean | = | + | | 0.107 | | 0.111 |
| | Std Dev | = | + | | 0.009 | | 0.013 |
| | $CV_2$ | = | + | | 0.084 | | 0.117 |
| | Recovery | = | + | | 99.1% | | 102% |
| 30 | 3.54 | | 0.089 | 3.05 | 0.104 | 3.54 | 0.104 |
| | 3.54 | | 0.076 | 3.05 | 0.103 | 3.54 | 0.091 |
| | 3.54 | | 0.085 | 3.05 | 0.102 | 3.54 | 0.104 |
| | 3.54 | | 0.082 | 3.05 | 0.097 | 3.54 | 0.103 |
| | N | = | 4 | | 4 | | 4 |
| | Mean | = | 0.083 | | 0.102 | | 0.101 |
| | Std Dev | = | 0.0055 | | 0.003 | | 0.006 |
| | $CV_2$ | = | 0.066 | | 0.031 | | 0.063 |
| | Recovery | = | 76.9% | | 94.0% | | 93.1% |

* Same as day 0 for room temperature
+ Due to poor precision and analytical difficulties, data are deleted from statistical analysis and are not presented graphically in Section 4.5.

Table 6

Humidity Test - $HN_3$
(0.5 × PEL & 25°C)

| % RH | 30 | 50 | 80 |
|---|---|---|---|
| ppm $HN_3$ Taken | 0.061 | 0.057 | 0.057 |
| ppm $HN_3$ Found | 0.068 | 0.053 | 0.057 |
| | 0.058 | 0.058 | 0.065 |
| | 0.063 | 0.053 | 0.047 |
| | 0.057 | 0.061 | 0.067 |
| | 0.062 | 0.056 | 0.046 |
| | 0.058 | 0.054 | 0.051 |
| | 0.062 | | |
| | 0.059 | | |
| N | 8 | 6 | 6 |
| Mean (ppm) | 0.061 | 0.056 | 0.056 |
| Std Dev (ppm) | 0.004 | 0.003 | 0.009 |
| CV | 0.060 | 0.057 | 0.163 |
| Ave Recovery | 100% | 98.0% | 97.4% |

At the 99% confidence level:

$F_{crit}$ = 6.11 $F_{calc}$ = 0.12 (2, 17 degrees of freedom)

$F_{crit} > F_{calc}$; therefore, no significant difference in results was noted across the humidity levels tested.

Humidity Test - $HN_3$
(1 × PEL & 25°C)

| % RH | 30 | 50 | 80 |
|---|---|---|---|

| | | | |
|---|---|---|---|
| ppm $HN_3$ Taken | 0.124 | 0.130 | 0.121 |
| ppm $HN_3$ Found | 0.122 | 0.129 | 0.119 |
| | 0.129 | 0.121 | 0.124 |
| | 0.131 | 0.135 | 0.118 |
| | 0.125 | 0.117 | 0.115 |
| | | 0.122 | 0.115 |
| | | 0.121 | 0.122 |
| N | 4 | 6 | 6 |
| Mean (ppm) | 0.127 | 0.124 | 0.119 |
| Std Dev (ppm) | 0.004 | 0.007 | 0.004 |
| CV | 0.032 | 0.053 | 0.031 |
| Ave Recovery | 102% | 95.5% | 98.2% |

At the 99% confidence level:

$F_{crit}$ = 6.70 $F_{calc}$ = 3.42 (2, 13 degrees of freedom)

$F_{crit} > F_{calc}$; therefore, no significant difference in results was noted across the humidity levels tested.

Humidity Test - $HN_3$
(2 × PEL & 25°C)

| % RH | 30 | 50 | 80 |
|---|---|---|---|
| ppm $HN_3$ Taken | 0.202 | 0.263 | 0.206 |
| ppm $HN_3$ Found | 0.203 | 0.259 | 0.218 |
| | 0.214 | 0.267 | 0.199 |
| | 0.202 | 0.252 | 0.213 |
| | 0.210 | 0.251 | 0.191 |
| | 0.200 | 0.276 | 0.182 |
| | 0.203 | 0.272 | 0.196 |

| | | | |
|---|---|---|---|
| | 0.215 | | |
| N | 7 | 6 | 6 |
| Mean (ppm) | 0.207 | 0.263 | 0.200 |
| Std Dev (ppm) | 0.006 | 0.010 | 0.014 |
| CV | 0.030 | 0.040 | 0.068 |
| Ave Recovery | 102% | 99.9% | 97.0% |

At the 99% confidence level:

$F_{crit}$ = 6.23 $F_{calc}$ = 2.11 (2, 16 degrees of freedom)

$F_{crit} > F_{calc}$; therefore, no significant difference in results was noted across the humidity levels tested.

Table 7
Qualitative and Quantitative Detection Limits (IUPAC Method)

| | ---------$HN_3$ (as $N_3^-$) Level----------- | | |
|---|---|---|---|
| Sample No. | 0.02 µg/mL PA | 0.05 µg/mL PA | 0.10 µg/mL PA |
| 1 | 5.07 | 15.19 | 42.23 |
| 2 | 5.31 | 17.03 | 36.72 |
| 3 | 4.65 | 14.10 | 40.02 |
| 4 | 4.78 | 14.87 | 36.29 |
| 5 | 4.16 | 12.35 | 39.73 |
| 6 | 4.42 | 14.41 | 40.21 |
| 7 | 5.61 | 13.44 | 38.18 |
| N | 7 | 7 | 7 |
| Mean | 4.86 | 14.48 | 39.05 |
| Std Dev | 0.507 | 1.468 | 2.108 |
| CV | 0.104 | 0.101 | 0.054 |

PA = Integrated Peak Area ($N_3^-$)/100,000

The blank and 0.01 mg/mL integrated peak areas, and their standard deviations (Std Dev) were all equal to zero.

---

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

Where:

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

k = 3 (Qualitative Detection Limit, 99.86% Confidence)

= 10 (Quantitative Detection Limit, 99.99% Confidence)

sd = standard deviation of the reagent blank (Rbl) readings.

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

$C_{ld}$ = 3(0.507)/438.6 = 0.00347 µg/mL as $N_3^-$ for the qualitative limit.

$C_{ld}$ = 10(0.507)/438.6 = 0.01156 µg/mL as $N_3^-$ for the quantitative limit.

Qualitative detection limit = 0.0104 µg $N_3^-$ (3-mL sample volume) or 0.001 ppm $HN_3$ (5-L air volume).

Quantitative detection limit = 0.0348 µg $N_3^-$ (3-mL sample volume) or 0.004 ppm $HN_3$ (5-L air volume).

Table 8a
Comparison Study - With/Without Pre-filter
(Known Concentration = 0.131 ppm $HN_3$)
(25°C, and 50% RH)

| | With Pre-filter | | Without Pre-filter | |
|---|---|---|---|---|
| Sample Set # | Air Vol, L | ppm $HN_3$ Found | Air Vol, L | ppm $HN_3$ Found |
| 1 | 3.41 | 0.124 | 3.38 | 0.141 |
| 2 | 3.41 | 0.140 | 3.38 | 0.138 |
| 3 | 3.41 | 0.134 | 3.38 | 0.131 |

| | | | | |
|---|---|---|---|---|
| 4 | 3.41 | 0.098* | 3.38 | 0.114 |
| N | | 3 | | 4 |
| Mean | | 0.133 | | 0.131 |
| Std Dev | | 0.008 | | 0.012 |
| CV | | 0.061 | | 0.092 |
| Recovery | | 101% | | 100% |

* Outlier

Notes:
a. A 37-mm PVC filter was used as the pre-filter in a polystyrene cassette.
b. Sampling Time = 5 min
c. Flow Rate = 0.825 to 0.829 L/min
d. Sample Solution Volume for Desorption = 3.0 mL

At the 99% confidence level:

$t_{crit}$ = 9.92 $t_{calc}$ = -0.615 (2 degrees of freedom)

$t_{crit} > t_{calc}$; therefore, no significant difference in results was noted across the two sets tested.

Table 8b
Comparison Study - With/Without Foam
(Known Concentration = 0.141 ppm $HN_3$)
(25°C, and 50% RH)

| | With Foam | | Without Foam | |
|---|---|---|---|---|
| Sample Set # | Air Vol, L | ppm $HN_3$ Found | Air Vol, L | ppm $HN_3$ Found |
| 1 | 3.35 | 0.129 | 3.43 | 0.155 |
| 2 | 3.35 | 0.140 | 3.43 | 0.135 |
| 3 | 3.35 | 0.138 | 3.43 | 0.140 |
| 4 | 3.35 | 0.155 | 3.43 | 0.154 |
| N | | 4 | | 4 |

| | | |
|---|---|---|
| Mean | 0.141 | 0.146 |
| Std Dev | 0.011 | 0.010 |
| CV | 0.077 | 0.069 |
| Recovery | 100% | 104% |

Notes:
a. Type II containing 150 mg-ISG glass jacket was used. The dimensions of the front portion of the glass jacket are 12-mm o.d., 10-mm i.d., and 25-mm long and is used for collecting azide particulate. The second part of the glass tube contains ISG and is used for collecting $HN_3$. The dimensions of the second part are 6-mm o.d., 4-mm i.d., and 50-mm long. Both ends of the sampling tube are sealed with plastic caps (see Method No. ID-200 for a graphic description of the Type II glass jacket used).
b. Foam analyzed after sampling contained 0.004 ppm as $HN_3$ (average).
c. Sampling Time = 5 min
d. Flow Rate = 0.627 to 0.787 L/min
e. Sample Solution Volume for Desorption = 3.0 mL

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At the 99% confidence level:

$t_{crit}$ = 5.84 $t_{calc}$ = -0.0055 (3 degrees of freedom)

$t_{crit} > t_{calc}$; therefore, no significant difference in results was noted across the two sets tested.

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**Block Diagram of the Laboratory Generation System**

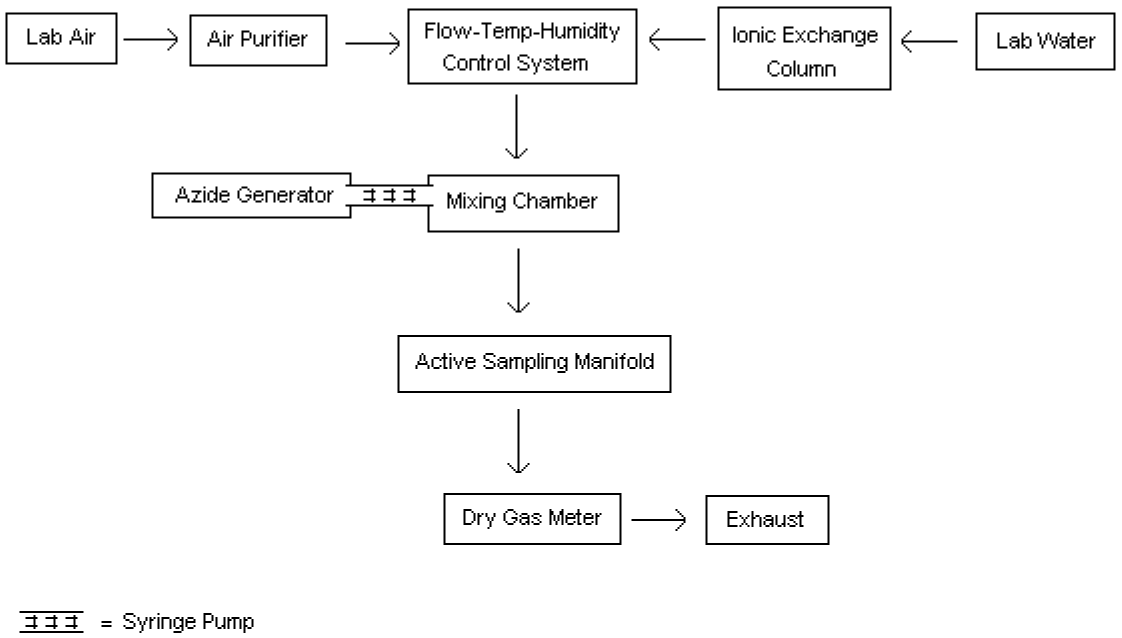


**Figure 1**

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The system shown above was used to generate dynamic test atmospheres. The system consists of four essential elements:

1. A flow-temperature-humidity control system,
2. An $HN_3$ vapor generating system,
3. A mixing chamber, and
4. An active sampling manifold.

Appendix

$$W_{HA} = (\mu g/mL\ N_3^-)(SV)(GF)_{HA}$$

$$\text{ppm } HN_3 = \frac{W_{HA} \times MV}{AV \times MW}$$

Where:

| | | |
|---|---|---|
| AV | = | Air volume |
| $W_{HA}$ | = | $\mu$g $HN_3$ |
| $(GF)_{HA}$, $HN_3/N_3^-$ | = | Gravimetric factor = 1.0238 |
| MV | = | Molar volume (L/mol) = 24.45 (25°C and 760 mmHg) |
| MW | = | Molecular weight for $HN_3$ = 43.0 (g/mol) |
| SV | = | Solution volume |
| $\mu$g/mL $N_3^-$ | = | Sample result taken from concentration-response curve |