

Nitrogen Dioxide in Workplace Atmospheres



Method Number:	ID-182 (This method supersedes ID-109)
Matrix:	Air
OSHA Permissible Exposure Limits	
Final Rule Limit:	1 ppm Short-Term Exposure Limit (STEL)
Transitional Limit:	5 ppm Ceiling
Collection Device:	Each sample is collected using a sampling tube containing triethanolamine-impregnated molecular sieve (TEA-IMS) and a calibrated sampling pump.
Recommended Sampling Rate:	0.20 L/min
Recommended Air Volume:	3.0 L (0.20 L/min for 15 min)
Analytical Procedure:	The sample is desorbed from the solid sorbent using a 1.5% triethanolamine (TEA) solution. Analysis is performed as nitrite (NO_2^-) by ion chromatography.
Detection Limit	
Qualitative:	0.07 ppm (3-L air sample)
Quantitative:	0.19 ppm (3-L air sample)
Precision and Accuracy	
Validation Range:	2.64 to 9.45 ppm
CV _T :	0.034
Bias:	+0.13
Overall Error:	±19.8%
Method Classification:	Validated Method
Chemist:	James Ku
Date (Date Revised):	December 1987 (May, 1991)

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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.

1. Introduction

This method describes the collection and analysis of airborne nitrogen dioxide (NO₂). Samples are taken in the breathing zone of workplace personnel and analysis is performed by ion chromatography (IC).

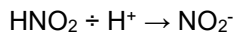
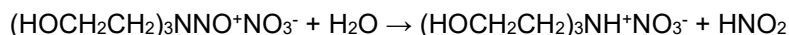
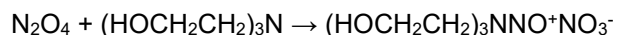
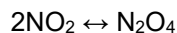
1.1. History

Previous methods of analysis for NO₂ involved collection of nitrogen dioxide in bubblers of triethanolamine (TEA) solution or a triethanolamine-impregnated molecular sieve (TEA-IMS) solid sorbent and TEA extraction (8.1). Nitrogen dioxide exposure was determined colorimetrically by the Griess-Saltzman reaction (8.1-8.3). This method, like most colorimetric procedures, can have significant interferences. A differential pulse polarographic (DPP) method (8.4) was later developed to improve sensitivity and decrease the potential for interferences. The sensitivity of the DPP method was adequate for measuring workplace concentrations of nitrogen dioxide; however, the nitrite ion is unstable at the pH range (pH 1-2) used during analysis (8.5).

Method no. ID-182 uses the collection principle of the TEA-IMS tube. The samples are analyzed by IC to determine NO₂ exposure.

1.2. Principle

A known volume of air is drawn through a sampling tube containing TEA-IMS. Nitrogen dioxide is trapped and converted to nitrite in the presence of TEA and water. Samples are desorbed using an aqueous TEA solution and analyzed as nitrite. The conversion mechanism of NO₂ gas to nitrite ion has been proposed by Gold (8.6). The following is Gold's proposal for the reaction of equivalent amounts of NO₂ and TEA in an aqueous solution:



Nitrogen dioxide disproportionates to nitrite and nitrate ions in the presence of TEA. The nitrite ion (NO₂⁻) formed from the above reaction can be analyzed via conventional analytical methods (8.1-8.5) including IC (8.7). The high background levels of nitrate found in commercial TEA-IMS sorbents ruled out further research to assess this NO₂⁻ TEA disproportionation product by IC.

This reaction path requires a stoichiometric factor of 0.5 for the conversion of gaseous NO₂ to NO₂⁻. Experiments indicate the proposed factor of 0.5 is seen only when NO₂ concentrations are greater than 10 ppm (8.6, 8.8-8.9). The conversion factor has been experimentally determined to average approximately 0.6 to 0.7 when concentrations are below 10 ppm (8.1-8.4, 8.6-8.9).

The deviation from ideal stoichiometry is believed to be due to other competing reactions; however, evidence to support this has not been found (8.6).

1.3. Advantages and Disadvantages

- 1.3.1. The analysis is simple, rapid, easily automated, and specific for the nitrite ion.
- 1.3.2. After sample preparation, nitrogen dioxide (as nitrite ion) can also be determined by polarographic or colorimetric analytical techniques (8.1-8.4).
- 1.3.3. Nitric oxide (NO) can also be sampled when using a three-tube sampling device (8.10). Sulfur dioxide may also be screened using the TEA-IMS sampling tube and similar analytical conditions (8.7).
- 1.3.4. A disadvantage is the potential interference from large amounts of soluble chloride salts present in commercial molecular sieve. Prior to TEA impregnation, the molecular sieve should be washed with deionized water to remove any soluble chloride salts.
- 1.3.5. Another disadvantage is the need for a concentration-dependent conversion factor when calculating results.

1.4. Physical Properties (8.11)

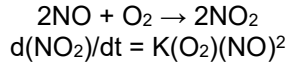
Nitrogen dioxide (CAS No. 10102-44-0), one of several oxides of nitrogen, is a reddish-brown or dark orange gas with a formula weight of 46.01. Its dimer, nitrogen tetroxide (N_2O_4), is colorless. At temperatures between -9.3 and 135 °C, NO_2 and N_2O_4 coexist as a mixture of gases. Below -9.3 °C, a colorless solid consisting of N_2O_4 is formed, while above 135 °C, the gas is mainly composed of NO_2 . Physical characteristics of NO_2 are:

Formula weight:	46.01
Specific gravity:	1.448 at 20 °C (liquid)
Melting point:	-9.3 °C
Boiling point:	21.15 °C
Vapor pressure:	96 KPa (720 mmHg) at 20 °C
Vapor density:	1.58 (air = 1)
Other characteristics:	strong oxidizer, corrosive, nonflammable
Synonyms:	dinitrogen tetroxide, nitrogen tetroxide, nitrogen peroxide, liquid dioxide

1.5. Some sources for potential nitrogen dioxide exposures are:

agricultural silos
arc or gas welding (esp. confined space operations)
electroplating plants
food and textile bleaching
jewelry manufacturing
nitric acid production nitrogen fertilizer production
nitro-explosive production
pickling plants

Nitrogen dioxide and nitric oxide usually exist together in industrial settings. Nitric oxide is reactive in air and produces NO_2 according to the following equations (8.11):



(K is a temperature dependent constant. At 20 °C, $K = 14.8 \times 10^9$)

An experimental approximation of the NO/NO₂ distribution found in various industrial operations is shown (8.11).

<u>Source</u>	<u>% NO₂</u>	<u>% NO</u>
Carbon arc	9	91
Oxyacetylene torch	8	92
Cellulose nitrate combustion	19	81
Diesel exhaust	35	65
Dynamite blast	52	48
Acid dipping	78	22

The potential for exposure to both NO₂ and NO should be considered because NO is easily oxidized to NO₂ and both oxides are likely to coexist in industrial settings.

1.6. Toxicology

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

1.6.1. Nitrogen dioxide is classified as a respiratory irritant and the route of exposure is mainly inhalation. The term silo-fillers' disease is associated with exposure to nitrogen dioxide as well as other nitrogen oxides.

Unlike the more soluble gases (e.g., chlorine, ammonia) that produce almost immediate upper respiratory tract irritation, symptoms of NO₂ exposure may be delayed for up to 12 hours. The lower solubility of NO₂ provides less warning and increases the potential for physiological damage when exposures occur.

1.6.2. The symptoms from mild exposures (<50 ppm) are generalized below (8.12-8.14):

- mucoïd or frothy sputum production
- cough
- painful breathing
- fever
- chest pains
- tachycardia
- increased breathing rate
- lymphocytosis

Exposures usually result in an increased susceptibility to respiratory infections. Changes in pulmonary function are evident when healthy subjects are exposed to 2 to 3 ppm NO₂ and can occur at far lower concentrations in asthmatic subjects.

More severe exposures (>50 ppm) are characterized by pulmonary edema, cyanosis, bronchiolitis obliterans, respiratory failure and death.

1.6.3. The LC50 (Lethal Concentration 50) for a 4-hour exposure is approximately 90 ppm NO₂.

2. Range, Detection Limit and Sensitivity (8.8)

2.1. This method was evaluated over the concentration range of 2.64 to 9.45 ppm. An air volume of 3 L and a flow rate of 0.2 L/min were used. Samples were taken for 15 min. Sample results were calculated using an average conversion relationship of:

$$1 \mu\text{g NO}_2 = 0.63 \mu\text{g NO}_2^-$$

At NO₂ concentrations above 10 ppm, the conversion factor has been shown to decrease, approaching a value of 0.5 (8.6, 8.8-8.9).

2.2. The qualitative detection limit was 0.08 µg/mL or 0.24 µg (as NO₂⁻) when using a 3-mL solution volume. This corresponds to 0.07 ppm NO₂ for a 3-L air volume.

2.3. The quantitative detection limit was 0.23 µg/mL or 0.69 µg (as NO₂⁻) when using a 3-mL solution volume. This corresponds to 0.19 ppm NO₂ for a 3-L air volume. A 50-µL sample loop and a detector setting of 3 microsiemens were used for both detection limit determinations.

2.4. The sensitivity of the analytical method was calculated from the slope of a linear working range curve (1 to 20 µg/mL nitrite). The sensitivity for this curve was 222,720 area units per 1 µg/mL (a Hewlett-Packard 3357 data reduction system was used, and 1 area unit = 0.25 microvolt-second).

3. Method Performance (8.8)

3.1. The pooled coefficient of variation (CV_T) for samples taken in the range of 2.64 to 9.45 ppm was 0.034. The method exhibited positive bias (+0.13); however, overall error is within acceptable limits at ±19.8%.

3.2. The collection efficiency at approximately 2 times the PEL was 97.3%. Samples were collected at a generation concentration of 9.45 ppm NO₂ for 15 min. Sample generation conditions were 50% RH and 25 °C.

3.3. Breakthrough tests were performed at 30% RH and a concentration of 21 ppm. Samples were collected for 15 min at a flow rate of 0.18 L/min. Breakthrough of NO₂ into a second sorbent tube at these parameters was 1.6% NO₂. This is within an acceptable limit of <5% breakthrough.

3.4. Samples can be stored at ambient (20 to 25 °C) laboratory conditions for a period of at least 29 days. Storage stability results show the mean of samples analyzed after 29 days was within ±5% of the mean of samples analyzed after one day of storage. Samples were stored on a laboratory bench.

4. Interferences

4.1. When other compounds are known or suspected to be present in the sampled air, such information should be transmitted to the laboratory with the sample.

4.2. Any compound having the same retention time as nitrite, when using the operating conditions described, is an interference.

4.3. Interferences may be minimized by changing the eluent concentration, and/or pump flow rate.

4.4. If there is reason to suspect an unresolvable interference, alternate polarographic or colorimetric methods can be used (8.1-8.4).

4.5. Contaminant anions normally found in molecular sieve, such as NO_3^- , SO_4^{2-} , and PO_4^{3-} , do not interfere. Large amounts (greater than 4 to 5 $\mu\text{g}/\text{mL}$) of Cl^- can interfere.

5. Sampling

5.1. Equipment

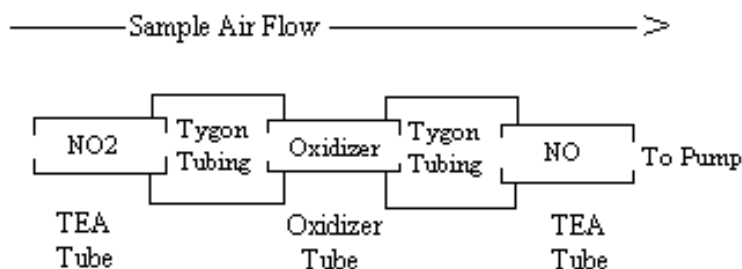
5.1.1. Personal sampling pumps capable of sampling within $\pm 5\%$ of the recommended flow rate of 0.2 L/min are used.

5.1.2. Two types of sampling tubes are commercially available (All molecular sieve used for tube packing should be washed with deionized water before impregnation with TEA).

a) One type is a two-section tube packed with a 400-mg TEA-IMS front and a 200-mg back-up section (NO_2 sampling tube, Cat. No. 226-40-02-special order, water-washed, SKC, Eighty Four, PA).

b) The other type, a three-tube sampling device (NO/NO_2 sampling tubes, Cat. No. 226-40-special order, water-washed, SKC, Eighty Four, PA) can be used to sample NO_2 and NO simultaneously or individually. The device consists of three flame-sealed glass tubes. Nitrogen dioxide is collected in the first tube which contains 400 mg TEA-IMS. Two other tubes, an oxidizer tube and another 400 mg TEA-IMS packed tube, are also included. The dimensions of each TEA-IMS tube are 7-mm o.d., 5-mm i.d., and 70-mm long. A 3-mm portion of silylated glass wool is placed in the front and rear of each tube. An oxidizer tube containing approximately 1 g of a chromate compound is used to convert NO to NO_2 . The dimensions of the oxidizer tube are 7-mm o.d., 5-mm i.d., and 110-mm long. When the three tubes are connected in series as shown below, NO_2 and NO can be collected simultaneously.

THREE-TUBE SAMPLING DEVICE



For further information regarding sampling for NO , see reference 8.10.

5.1.3. A stopwatch and bubble tube or meter are used to calibrate pumps. A sampling tube or device is placed in-line during flow rate calibration.

5.1.4. Various lengths of Tygon tubing are used to connect sampling tubes to pumps.

5.2. Sampling Procedure

Note: If sampling for both NO₂ and NO is necessary, two separate pumps and sampling devices should be used. The differences in OSHA Final Rule PELs (NO₂ is a STEL and NO is a TWA PEL) and flow rates dictates a need for a singular assessment of NO₂. Nitric oxide is collected at a flow rate **not to exceed** 0.025 L/min (8.9-8.10) and a three-tube device must be used. Nitrogen dioxide can be collected at this flow rate; however, a longer sampling time will be necessary to collect a detectable amount of NO₂ than for a short-term measurement. Also, NO₂ concentrations may vary widely during sampling periods as long as 4 hours for NO. The three-tube sampling device will not reflect the varying concentration. Therefore, it is recommended to sample at 0.2 L/min for 15-min intervals using a single or two section tube **for NO₂**. A separate three-tube device and pump is then used **for NO** sampling. The front tube of the device can be submitted for NO₂ analysis; however, results from this front section may not represent short-term exposures.

5.2.1. Calibrate the sampling pumps at either recommended flow rate listed in Section 5.2.4.

5.2.2. Connect the sampling tube or device to the pump. The different sampling schemes are listed below:

- a) **Sampling for NO₂ only:** A single TEA-IMS tube taken from the three-tube sampling device (Section 5.1.2, part b) or the two-section tube (Section 5.1.2, part a) can be used. If the two-section tube is used, sampled air should enter the 400 mg section first.
- b) **Sampling for both NO and NO₂:** The three-tube device (Section 5.1.2, part b) is used. Label the first tube "NO₂". The tube following the oxidizer section is labeled "NO". Also consult reference 8.10.

5.2.3. Place the sampling tube or device in the breathing zone of the employee.

5.2.4. Sample with pre-calibrated pumps at the listed flow rates and sampling times:

- a) **For NO₂ only:** 0.2 L/min for at least 15 min per sample.
- b) **For both NO and NO₂:** 0.025 L/min for 4 h per sample. Also consult reference 8.10.

Nitrogen dioxide results from extended sampling times (>15 min) may not reflect short-term exposures.

5.2.5. The minimum recommended total air volume for collecting NO₂ is 3 L.

6. Analysis

6.1. Precautions

6.1.1. Refer to instrument and standard operating procedure (SOP) (8.15) manuals for proper operation.

6.1.2. Observe laboratory safety regulations and practices.

6.1.3. Sulfuric acid (H₂SO₄) can cause severe burns. Wear protective gloves and eyewear when using concentrated H₂SO₄.

6.2. Equipment

- 6.2.1. Ion chromatograph (Model 2010 or 4000, 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: Ion chromatograph interfaced to a data reduction and control system (Autolon 400 or 450 System, Dionex).
- 6.2.4. Printer.
- 6.2.5. Separator and guard columns, anion (Model HPIC-AS4A and AG4A, Dionex).
- 6.2.6. Micro-membrane suppressor, anion (Model AMMS-1, Dionex).
- 6.2.7. Disposable syringes (1 mL) and pre-filters.

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

- 6.2.8. Erlenmeyer flasks, 25-mL, or scintillation vials, 20-mL.
 - 6.2.9. Miscellaneous volumetric glassware: Micropipettes, volumetric flasks, graduated cylinders, and beakers.
 - 6.2.10. Analytical balance (0.01 mg).
- 6.3. Reagents - All chemicals should be at least reagent grade.
- 6.3.1. Deionized water (DI H₂O) with a specific conductance of less than 10 microsiemens.
 - 6.3.2. Triethanolamine [(HOCH₂CH₂)₃N]
 - Sodium carbonate (Na₂CO₃)
 - Sodium bicarbonate (NaHCO₃)
 - Sulfuric acid (H₂SO₄, concentrated 95 to 98%)
 - Sodium nitrite (NaNO₂)
 - 6.3.3. Liquid desorber (1.5% TEA):
 - Dissolve 15 g TEA in a 1-L volumetric flask which contains approximately 500 mL DI H₂O. Add 0.5 mL n-butanol and then dilute to volume with DI H₂O.
 - 6.3.4. Eluent (2.0 mM Na₂CO₃/1.0 mM NaHCO₃):
 - Dissolve 0.848 g Na₂CO₃ and 0.336 g NaHCO₃ in 4.0 L of DI H₂O.
 - 6.3.5. Regeneration solution (0.02 N H₂SO₄):
 - Place 1.14 mL concentrated H₂SO₄ into a 2-L volumetric flask which contains about 500 mL DI H₂O. Dilute to volume with DI H₂O.
 - 6.3.6. Nitrite stock standard (1,000 µg/mL):

Dissolve 1.5000 g NaNO₂ and dilute to the mark in a 1-L volumetric flask with DI H₂O. Prepare every 3 months.

6.3.7. Nitrite standard (100 µg/mL):

Dilute 10 mL of the 1,000 µg/mL nitrite stock standard to 100 mL with liquid desorber. Prepare monthly.

6.3.8. Nitrite standard (10 µg/mL):

Dilute 10 mL of the 100 µg/mL nitrite stock standard to 100 mL with liquid desorber. Prepare weekly.

6.3.9. Nitrite standard (1 µg/mL):

Dilute 10 mL of the 10 µg/mL nitrite stock standard to 100 mL with liquid desorber. Prepare daily.

6.4. Working Standard Preparation

6.4.1. Nitrite working standards (10-mL final volumes) may be prepared in the ranges specified below:

Working Std µg/mL	Standard Solution µg/mL	Aliquot mL
0.5	1	5
1	1	*
3	10	3
6	10	6
10	10	*
20	100	2

* Already prepared in Section 6.3

6.4.2. Pipette appropriate aliquots of standard solutions (prepared in Section 6.3) into 10-mL volumetric flasks and dilute to volume with liquid desorber.

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.

6.4.4. Prepare a reagent blank from the liquid desorber solution.

6.5. Sample Preparation

Note: For NO sample analysis and result calculations, see reference 8.10.

6.5.1. Clean the 25-mL Erlenmeyer flasks or scintillation vials by rinsing with DI H₂O.

6.5.2. Carefully remove the glass wool plugs from the sample tubes, making sure that no sorbent is lost in the process. If the two-section tube was used for sampling, transfer each TEA-IMS section to individual 25-mL Erlenmeyer flasks or scintillation vials. Analyze these two sections separately. If a single section tube was used, transfer that section to an individual 25-mL Erlenmeyer flask or scintillation vial.

- 6.5.3. Add 3 mL of liquid desorber to each flask or vial, shake vigorously for about 30 s and allow the solution to settle for at least 1 h.
- 6.5.4. If the sample solutions contain suspended particulate, remove the particles using a pre-filter and syringe. Fill the 0.5-mL automatic sampler vials with sample solutions and push a 0.5-mL filter cap into each vial. Label each vial.
- 6.5.5. Load the automatic sampler with labeled samples, standards and blanks.

6.6. Analytical Procedure

Set up the ion chromatograph and analyze the samples in accordance with the SOP (8.15). Typical operating conditions for equipment mentioned in Section 6.2 are listed below.

Ion chromatograph

Eluent: 2.0 mM Na₂CO₃/1.0 mM NaHCO₃
 Column temperature: ambient
 Sample injection loop: 50 µL

Pump

Pump pressure: approximately 1,000 psi
 Flow rate: 2 mL/min

Chromatogram

Run time: 6 min
 Average retention time: approximately 2 min

7. Calculations

- 7.1. Obtain hard copies of chromatograms from a printer. A typical chromatogram is shown in Figure 1.
- 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.
- 7.3. Blank correct the samples by subtracting the µg/mL NO₂⁻ found in the blank from the µg/mL NO₂⁻ found in the samples. If a different solution volume was used for blanks and samples, use total micrograms NO₂⁻ to blank correct.
- 7.4. Calculate the concentration of nitrogen dioxide in each air sample in ppm. A concentration-dependent conversion factor is used. The equation is:

$$ppm NO_2 = \frac{Molar Volume \times ug/mL \times NO_2^- \times Solution Volume \times Conversion}{Forumula weight \times Air Volume}$$

where:

Molar Volume = 24.45 (25 °C and 760 mmHg)

µg/mL NO₂⁻ = blank corrected sample result

Formula Weight (NO₂) = 46.01

Conversion = varies with concentration

The conversion of gaseous NO₂ to NO₂⁻ is concentration-dependent and should be calculated using one of the equations given below:

Below 10 ppm NO₂

From 0 to 10 ppm, the average relationship has been experimentally determined to be (8.1-8.4, 8.6-8.9):

$$1 \mu\text{g NO}_2 \text{ (gas)} = 0.63 \mu\text{g NO}_2$$

or conversely:

$$1 \mu\text{g NO}_2^- = 1.587 \mu\text{g NO}_2 \text{ (gas)}$$

Simplifying the equation and using a 3-mL sample volume gives:

$$\text{ppm NO}_2 = \frac{\text{ug/mL} \times \text{NO}_2^- \times 3 \text{ mL} \times 0.0843}{\text{Air Volume (L)}}$$

Above 10 ppm NO₂

Above 10 ppm NO₂, the expected stoichiometric factor of 0.5 mole of nitrite to 1 mole of nitrogen dioxide gas is seen (8.6, 8.8-8.9). Therefore, the following calculation should be used for sample results above 10 ppm and a 3-mL sample volume:

$$\text{ppm NO}_2 = \frac{\text{ug/mL} \times \text{NO}_2^- \times 3 \text{ mL} \times 1.0633}{\text{Air Volume (L)}}$$

7.5. Reporting Results

Report all results to the industrial hygienist as ppm nitrogen dioxide.

8. References

- 8.1. National Institute for Occupational Safety and Health: NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4 (HEW/NIOSH Pub. No. 78-175). Cincinnati, OH, 1978.
- 8.2. Saltzman, B.E.: Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere. Anal. Chem. **26**:1949 (1954).
- 8.3. Blacker, J.H.: Triethanolamine for Collecting Nitrogen Dioxide in the TLV Range. Am. Ind. Hyg. Assoc. J. **34**:390 (1973).
- 8.4. Occupational Safety and Health Administration Analytical Laboratory: OSHA Analytical Methods Manual (USDOL/OSHA-SLCAL Method No. ID-109). Cincinnati, OH: American Conference of Governmental Industrial Hygienists (Pub. No. ISBN: 0-936712-66-X), 1985.
- 8.5. Chang, S.K., R. Kozenianskas and G.W. Harrington: Determination of Nitrite Ion Using Differential Pulse Polarography. Anal. Chem. **49**:2272-2275 (1977).
- 8.6. Gold, A.: Stoichiometry of Nitrogen Dioxide Determination in Triethanolamine Trapping Solution. Anal. Chem. **49**:1448-50 (1977).
- 8.7. Vinjamoori, D.V. and Chaur-Sun Ling: Personal Monitoring Method for Nitrogen Dioxide and Sulfur Dioxide with Solid Sorbent Sampling and Ion Chromatographic Determination. Anal. Chem. **53**:1689-1691 (1981).

- 8.8. Occupational Safety and Health Administration Technical Center: Nitrogen Dioxide Backup Report (ID-182), by J.C. Ku. Salt Lake City, UT. Revised 1991.
- 8.9. Occupational Safety and Health Administration Technical Center: Nitric Oxide Backup Data Report (ID-190), by J.C. Ku (USDOL/OSHA-SLTC Method No. ID-190). Salt Lake City, UT, Revised 1991.
- 8.10. Occupational Safety and Health Administration Technical Center: Nitric Oxide in Workplace Atmospheres, by J.C. Ku (USDOL/OSHA-SLTC Method No. ID-190). Salt Lake City, UT. Revised 1991.
- 8.11. National Institute for Occupational Safety and Health: Criteria for a Recommended Standard...Occupational Exposure to Oxides of Nitrogen (Nitrogen Dioxide and Nitric Oxide) (HEW/NIOSH Pub. No. 76-149). Cincinnati, OH, 1976.
- 8.12. Berkow, R. and JH. Talbott, ed.: The Merck Manual. 13th ed. Rahway, NJ: Merck, Sharp and Dohme Research Laboratories, 1977. pp. 629-630.
- 8.13. Proctor, N.B. and J.P. Hughes: Chemical Hazards of the Workplace. Philadelphia, PA: J.B. Lippincott Company, 1978. pp. 382-383.
- 8.14. American Conference of Governmental Industrial Hygienists: Documentation of the Threshold Limit Values and Biological Exposure Indices. 5th ed. Cincinnati, OH: ACGIH, 1986. pp. 435-436.
- 8.15. Occupational Safety and Health Administration Technical Center: Standard Operating Procedure-Ion Chromatography. Salt Lake City, UT. In progress (unpublished).

Chromatogram of a 10 µg/mL Nitrate Standard in 1.5% TEA Solution

Peak Num	Ret Time	Peak Name	Area
1	0.90		1.778e+004
2	1.15		1.965e+004
3	1.50		2.214e+004
4	1.80	chloride	3.476e+003
5	2.13	nitrite	8.886e+004
6	4.18		3.600e+003

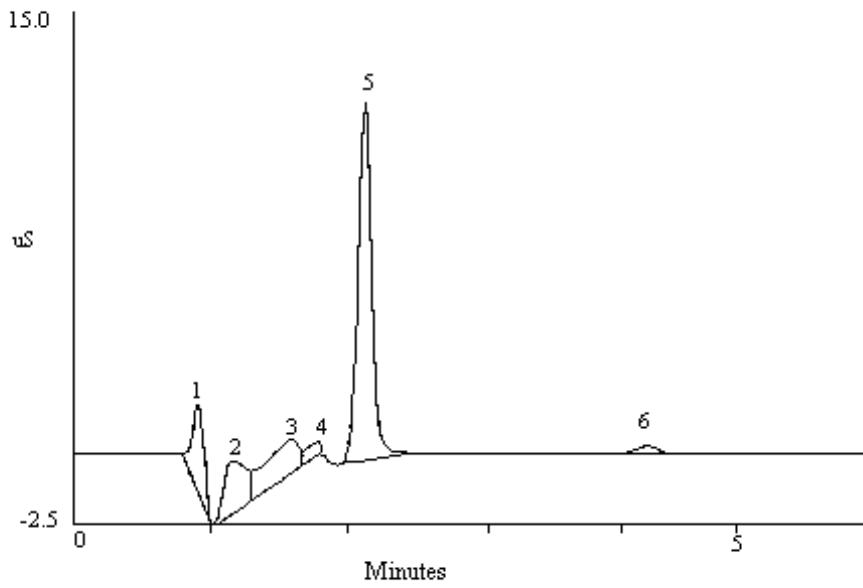


Figure 1

Nitrogen Dioxide Backup Data Report

Introduction

The general procedure for the air sample collection and analysis of nitrogen dioxide (NO₂) is described in OSHA Method No. ID-182 (11.1.). In the past, NO₂ was collected using a combination tube consisting of triethanolamine-impregnated molecular sieve (TEA-IMS). Nitrite contamination of the TEA-IMS was occasionally noted, was lot dependent, and highly variable. Air samples were taken with a flow rate of less than 0.05 L/min. Analysis was performed by either colorimetric or polarographic methods.

Presently, it is required to water-wash the molecular sieve before triethanolamine (TEA) impregnation to remove any soluble salts that may contribute to background measurement or act as an interference (i.e. nitrite or soluble chloride salts). The evaluation of Method No. ID-182 examines the use of the combination tube, and a three-tube sampling device at a flow rate of approximately 0.2 L/min. The four-fold increase in sample flow rate during collection should assist in detecting low levels of NO₂ and help minimize any impact from sorbent contamination. Analysis is performed by ion chromatography (IC).

This method was evaluated when the Permissible Exposure Limit (PEL) was a 5 ppm Ceiling. The OSHA Final Rule PEL for NO₂ is currently 1 ppm. A 15-min sampling time was used. Short descriptions of the components used for the evaluation are listed below.

Generation System

All generation of nitrogen dioxide test atmospheres, and hence all experiments, with one exception, were performed using the equipment shown in Figure 1. The detection limit study did not use a test atmosphere generation for sample spiking and collection. Instead, samples were spiked with solutions of sodium nitrite.

Nitrogen dioxide permeation tubes (Thermedics Inc., Woburn, MA) were used as the contaminant source for all of the generation experiments except the conversion factor experiment. A cylinder of nitric oxide (NO) in nitrogen and oxidizer tubes were used to determine conversion factors. Permeation rates during the other experiments were determined by measuring the weight loss of three permeation tubes over a given period of time. A constant temperature of 35 °C was used. As shown below, the calculated overall NO₂ permeation rate for the three tubes was 89.09 µg/min.

Time Elapsed (min)	Weight Loss (µg)	Diffusion Rate (µg/min)
4,335	387,600	89.41
5,700	513,400	90.07
10,105	904,200	89.48
10,095	882,100	87.38

Ave. 89.09 ± 1.17 µg/min

The NO₂ produced from the permeation source was diluted with a small amount of filtered air and then 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. A Teflon sampling manifold was attached to the mixing chamber. Flow rates for the diluent air were determined using a dry test meter. Contaminant gas flows were measured using mass flow controllers and soap bubble flowmeters.

Sampling Media

Three different TEA-IMS sampling systems were commercially available for NO₂ sampling at the beginning of the evaluation. The three devices are designed to simultaneously collect NO₂ and nitric oxide (NO). Preliminary studies conducted on the three different systems indicated the SKC collection device (1) listed below was the most suitable sampling device to collect NO and NO₂. A short description of each device is listed:

1. NO₂-NO collection device (Cat. No. 226-40, SKC, Eighty Four, PA):

The sampling device consists of three separate glass tubes, two TEA-IMS tubes and an oxidizer tube. Each glass tube is flame sealed. Both sample collection tubes consist of 400 mg TEA-IMS. The oxidizer contains approximately 1 g of a chromate compound. Either TEA-IMS tube can be used separately to monitor NO₂. When sampling for both NO and NO₂, the three tubes are connected with Tygon tubing such that the oxidizer tube is placed between the two TEA-IMS sampling tubes. The tubes used during the experiments were from lot no. 374.

2. SKC combination tube (Cat. No. 226-40 discontinued, SKC):

This combination tube contained all three sections in a single tube. Two 400 mg sections of TEA-IMS were separated by an 800 mg oxidizer section. This tube has been discontinued by SKC and replaced with the device mentioned above. The tubes used were from lot no. 306.

3. Supelco combination tube (Supelco, Bellefonte, PA):

This tube is similar in construction to the SKC lot no. 306 sampling tube (2) listed above with one exception. The Supelco tube uses a smaller mesh size of molecular sieve. Lot no. 582-99 was used for a Sampling and Analysis experiment.

SKC collection devices (1) and (2) listed above are identical except device (1) has a physical segregation of sorbents and oxidizer.

Due to low recoveries found during a preliminary study with Supelco sampling tubes, these tubes were excluded from the experiments.

Sample Collection

Air samples were collected from the Teflon manifold using calibrated Du Pont model P125 low flow pumps (flow rates of 0.175-0.200 L/min) for all experiments except for the Desorption Efficiency (DE) (Analysis - Section 1) determination. This experiment used low flow pumps to spike the TEA-IMS material with gaseous NO₂. The analysis experiment was designed to determine the amount of gas collected and not necessarily the sampling capability at this flow rate. A flow rate of 0.010 L/min with SKC Model 222-3-10 low flow pumps were used for the DE study.

Sample Analysis

Samples prepared for all experiments were analyzed by IC using the conditions specified in the method (11.1.). For the conversion of NO₂ to nitrite ion, a conversion factor (C.F.) of 0.72 had been proposed (11.2.) to use in result calculations. Later experiments revealed an average C.F. of 0.63 (11.3.-11.5.). A C.F. of 0.63 was used for all air sample experiments in this evaluation which were performed below 10 ppm NO₂.

Evaluation

The following experiments were performed for the evaluation of Method No. ID-182:

1. Analysis - (DE) of spiked samples
2. Sampling and Analysis - generation and analysis of NO₂ samples
3. Collection efficiency and breakthrough of TEA-IMS sampling tubes
4. Storage stability of sampling tubes
5. Sampling at different humidities
6. Analytical method comparison
7. Analytical detection limit determinations
8. Determination of conversion factor for NO₂ concentrations of 10 to 200 ppm. The preliminary sampling and analysis experiment using Supelco tubes is discussed in Section 9.

A statistical protocol (11.6.) was used to evaluate results. Data were subjected to the Bartlett's (11.7.) and an Outlier test (11.8.) to determine homogeneity of variance and identify any extraneous data.

1. Analysis (Desorption Efficiency, DE)

Procedure: A total of 20 spiked samples (8 samples at 0.5 and 6 samples at 1 and 2 times the Transitional PEL) were prepared and analyzed. Samples were prepared by spiking known amounts of NO₂ gas into TEA-IMS solid sorbent tubes. The spiked concentrations were approximately 2.5, 5.0, and 10 ppm of nitrogen dioxide. These concentrations are about 0.5, 1, and 2 times the OSHA Transitional PEL. Recoveries at these levels represent the analytical DE. Results also provide information regarding the extent of variability for the analytical portion of the method. Details for this experiment are discussed below:

1. SKC lot no. 374 sampling tubes were used.
2. Known NO₂ gas concentrations were prepared by using a ten-fold dilution of the NO₂ permeation source with tempered air (50% RH and 25 °C). Samples were dynamically spiked using calibrated SKC low flow rate pumps. The pumps slowly drew the diluted NO₂ contaminant gas into the TEA-IMS tubes. Samples were taken for measured time periods at a flow rate of approximately 0.010 L/min.

Results: The results of the analysis study are presented in Table 1. All data passed the Bartlett's test. One result tested as an outlier and was omitted. Results were pooled. The data (Table 1) indicates acceptable precision and accuracy (11.6.) for the analytical portion of the method and does not indicate a need for a desorption correction factor. The coefficient of variation for analysis (CV1) was 0.021 and the average analytical or spiked recovery was 106%.

2. Sampling and Analysis

Procedure: A total of 18 samples (6 samples at each of the three test levels) were collected from dynamically generated test atmospheres and analyzed. Generation and analysis of NO₂ was the same as mentioned in the Introduction. Sample results from the dynamic generation provide the overall error and precision of the sampling and analytical method. Overall error should be $\pm 25\%$ and was calculated using the following equation (11.6.):

$$\text{Overall error} = \pm [|\text{mean bias}| + 2\text{CVT}] \times 100\%$$

1. SKC sampling tubes, lot no. 306, were used for this experiment.
2. Samples were taken for 15-min sampling periods at concentrations of approximately 0.5, 1, and 2 times the OSHA Transitional PEL. The relative humidity and temperature of the generation system were set at 50% and 25 °C.

Results: The results of the sampling and analysis experiment are shown in Table 2. The sampling and analysis data also show acceptable precision and accuracy (11.6.). All data passed both the outlier and Bartlett's test and results were pooled. The pooled coefficients of variation for spiked CV1 (pooled), generated CV2 (pooled) samples, as well as the overall CVT (pooled), are as follows:

$$\text{CV1 (pooled)} = 0.021 \quad \text{CV2 (pooled)} = 0.033 \quad \text{CVT (pooled)} = 0.034$$

The overall bias was 13% high. Overall error was acceptable (< ±25%) and was ±19.8%.

3. Collection Efficiency and Breakthrough

3.1. Collection Efficiency

Procedure: Samples were generated to measure the sorbent collection efficiency at about 9.5 ppm NO₂.

- 3.1.1. SKC sampling tubes, lot no. 306, were used to collect the NO₂ at 50% RH and 25 °C. These were the combination tubes; each glass tube contained two sections of TEA-IMS separated by an oxidizer section.
- 3.1.2. Using the same generation system described in the Introduction, six samples were collected at 2 times the OSHA Transitional PEL for 15 min.
- 3.1.3. The amount of NO₂ vapor collected in the first and second sections of the tubes was measured. The collection efficiency was calculated by dividing the amount collected in the first solid-sorbent section by the total amount of NO₂ collected in both sections.

Results: Results are reported in Table 3. Collection efficiency was adequate at two times the Transitional PEL with an average recovery of 97%.

3.2. Breakthrough

Procedure: Samples were generated at a concentration greater than the evaluation levels to determine the extent of NO₂ breakthrough from the first solid sorbent tube into a second tube. The calculated breakthrough should be less than 5%.

- 3.2.1. Four sampling tubes (SKC lot no. 374) were connected to backup tubes and then to sampling pumps. Air samples were collected for 15 min at a concentration of approximately 4 times the Transitional PEL. The generation system was set at 30% RH and 25 °C. The low humidity level was used as a "worst case" test since the presence of water is necessary for the conversion reaction of NO₂ to NO₂⁻ to proceed (11.1., 11.3.).
- 3.2.2. Breakthrough was assessed by analyzing both tubes and dividing the amount collected in the second solid-sorbent tube by the total amount collected in both sections.

Results: The amount of breakthrough is shown in Table 3. Breakthrough studies indicate the sorbent tube capacity for NO₂ is adequate for air concentrations at least to 21 ppm (using air

volumes and flow rates described). Small amounts of NO₂ were detected on the backup tubes during both collection efficiency and breakthrough studies. This could be from contamination rather than actual breakthrough. Although sample results are blank corrected, blank readings can be variable (see Section 7 and Table 7 for further information regarding blanks). Regardless of blank contamination or breakthrough, the breakthrough recoveries for both studies are less than 5% and are considered acceptable.

4. Storage Stability

Procedure: A study was conducted to determine any effects on storage of TEA-IMS samples containing known amounts of NO₂. A storage period of approximately 1 month was used. The procedure used is discussed below:

- 4.1. The determination was performed using SKC lot no. 306 tubes.
- 4.2. Twenty-four samples were generated at the OSHA Transitional PEL as described in the Introduction.
- 4.3. These samples were stored at 20 to 25 °C and were placed laboratory bench for the duration of the storage period.
- 4.4. Six samples were analyzed after 1, 5, 15, and 29 days.

Results: The results of the storage stability study are shown in Table 4. Collected samples are stable at room temperature. The mean of samples analyzed after 29 days was within ±5% of the mean of samples analyzed after one day. Samples may be stored in normal environmental conditions found in a laboratory setting for a period of 29 days after sampling without producing a significant change in results.

5. Humidity Study

Procedure: A study was conducted to evaluate any effects on recovery when sampling at different humidities. A contaminant flow conditioned at different relative humidities and a constant temperature of 25 °C was generated using the system described in the Introduction. Relative humidities of 30, 50, and 80% were used. SKC lot no. 374 tubes were used and six samples were generated at each humidity level.

Results: Results are shown in Table 5. Data from sampling at different humidities displayed no apparent effect on sampling efficiency. As shown in Table 5, an analysis of variance (F test) was performed on the data to determine if any significant difference existed in different humidity group results. The average recovery across the three different humidity levels was also considered. The calculated F value is below the critical value and a significant effect from humidity does not appear to exist. Evidence of a slight increase in average recovery is apparent with an increase in humidity. However, the increase is within the variability of the method and also does not appear as significant. Therefore, the humidity study did not reveal a significant difference in recoveries or variance when sampling at 30, 50, and 80% RH (25 °C).

6. Comparison of Analytical Methods

The IC method was compared to a reference method to determine if any significant disagreement existed between the 2 methods. The previous analytical method, the differential pulse polarographic

(DPP) procedure (11.9.), was used as the reference analytical method. TEA-IMS samples were taken using the generation system described in the Introduction.

Procedure: Eighteen samples were generated and analyzed by IC. Since both analytical procedures use the same desorbing solution [(1.5% triethanolamine (TEA)], an aliquot was taken from each sample and analyzed by the polarographic method.

Results: A linear regression comparison of the two methods is shown in Figure 2 (the dotted line shown in Figure 2 represents ideal agreement between the two methods. The solid line represents the observed agreement). Results of the comparison between the IC and DPP method are also shown in Table 6. The comparison of the DPP and IC analytical methods show excellent correlation and agreement. The correlation coefficient (r) of 0.99 and a slope value of 1.0194 ± 0.0295 are very close to ideal values. An r and slope value equal to 1 would indicate ideal correlation and agreement between the two analytical methods. Over the concentration range tested the IC method results show an increase of 1.9% when compared to polarographic method results. The slightly higher recoveries of the IC procedure indicate that some of the bias noted (Section 2) can be attributed to the analytical portion of the method. The background levels inherent in the treated sorbent and erratic blank readings probably contribute to the positive bias also.

7. Analytical Detection Limits

Procedure: Qualitative and quantitative detection limits were determined by analyzing low concentration samples and blanks. The samples were prepared by spiking solutions containing 3 mL of 1.5% TEA with sodium nitrite solutions. The spiking was performed using a calibrated micropipette. Samples and blanks were analyzed using a 50 μ L sample injection loop and a conductivity cell sensitivity range setting of 3 microsiemens.

7.1. Qualitative detection limit: The Rank Sum Test (11.1.) was used for the determination of the qualitative detection limit of the IC analysis of NO_2 (as nitrite).

7.2. Quantitative detection limit: The International Union of Pure and Applied Chemistry (IUPAC) detection limit equation (11.11.) was used to calculate the detection limit.

Results: The results are listed in Table 7 and graphically displayed in Figure 3. The qualitative detection limit is 0.07 ppm NO_2 . The quantitative detection limit is 0.19 ppm NO_2 . A 50 μ L sample injection loop was used for all analyses in this evaluation. If necessary, a larger sample loop can be used to achieve a lower limit of detection. In the past, blank contamination was a serious problem and consequently caused high detection limits; blank levels were occasionally 0.5 to 1 times the Transitional PEL when using a 0.05 L/min flow rate for calculations. Soluble chloride salts can also elevate the detection limit. If the amount of chloride in the sample is large ($>5 \mu\text{g/mL}$), the nitrite ion appears as a shoulder on the chloride peak during IC analysis. Using the data reduction system described in Section 2 of the method (11.1.), chloride peak areas from non-water washed TEA-IMS tubes were 5 times greater than the water-washed sorbent. Nitrite peaks appeared as shoulders on the chloride peaks of the non-water washed sorbent. Water-washing decreased the chloride content to the point where good separation was noted between the chloride and nitrite peaks.

8. Conversion Factor (C.F.)

As described in OSHA Method No. ID-182 (11.1.), the proposed factor for the conversion of NO_2 gas to the nitrite ion is concentration dependent. If the reaction is stoichiometric, a C.F. of 0.5 would be

seen experimentally. In practice, however, this is not the case. For concentrations below 10 ppm, the average C.F. is 0.6 to 0.7 as reported by Morgan et. al. (11.12.), in a previous study (11.9.), and by numerous others (11.2-11.5.). For concentrations of 0 to 10 ppm NO₂, a factor of 0.63 was adopted by OSHA (11.9.) and NIOSH (11.13.). The factor was not well defined at higher concentrations and needed further evaluation. The following procedure was used to experimentally determine the C.F. for concentrations greater than 10 ppm:

- 8.1. A cylinder of NO in nitrogen (Air Products Co., 1.05% NO) was used as the contaminant source. The rapid depletion of the NO₂ permeation tubes precluded their use for this experiment. The same generation system shown in Figure 1 was used with the gas cylinder replacing the permeation tubes as the contaminant source. The NO₂ was produced by flowing a diluted NO mixture through oxidizer sections, which converted the NO to NO₂ before collection.
- 8.2. The generation system was set at 50% RH and 25 °C.
- 8.3. Samples were taken using impingers containing 1.5% TEA solutions for variable time periods at different concentration ranges. These TEA solutions were used in an attempt to avoid any extraneous background contribution from solid sorbent desorption or intrinsic contamination from the tubes. Samples were taken at a flow rate of 0.025 L/min to assure complete oxidation of the NO and to provide sufficient residence time of NO₂ in the TEA solutions.

Results: The results for C.F. calculations from 10 to 200 ppm are listed in Table 8. Data in Table 8 show the conversion factors for NO₂ concentrations from 10 to 200 ppm. The conversion factor for the 10 to 100 ppm concentration range averaged 0.50; at about 200 ppm the factor was 0.37. Further work may be necessary to determine why the factor decreased at the 200 ppm level. Another study indicated no breakthrough of NO at this concentration (11.14.). Previous sample results and the toxicology of NO₂ indicate a 200 ppm NO₂ sample collected in an industrial setting is unlikely. A correction factor and further work at this concentration level was not pursued for these reasons. The conversion factor is further discussed in reference 11.14.

9. Sampling and Analysis - Supelco Tubes

A preliminary evaluation of the combination tube manufactured by Supelco was conducted using the same conditions and equipment mentioned in the Introduction. Samples were collected using the procedure mentioned in Section 2. Results are listed in Table 9. This data indicates a sample loss of approximately 30% when sampling at approximately 0.2 L/min. The loss could be associated with a difference in mesh size (Supelco tubes contain a smaller mesh molecular sieve than SKC tubes), flow rate differences or a poorly prepared lot. The original methodology for sampling NO₂/NO with this type of tube specified a flow rate of less than or equal to 0.05 L/min. The four-fold increase in flow rate may be causing premature breakthrough. The residence time of the sampled gas may not be sufficient at 0.2 L/min for this tube.

10. Discussion

Two different lots of SKC tubes were used for the evaluation. The combination tube consisting of all three sections in a single tube (lot no. 306) was commercially available at the beginning of the evaluation. This tube was used for the sampling and analysis, collection efficiency, and storage stability experiments. Design changes were instituted and a three tube collection device was produced to offer greater convenience when sampling NO₂ or both NO and NO₂ simultaneously. The three-tube

collection device, lot no. 374, was used for the remaining studies. The two SKC devices are identical except the sorbent and oxidant are contained in three separate glass tubes for the three tube device.

The data generated during the evaluation of the method indicates an acceptable alternative to the polarographic method. The ion chromatographic method offers an accurate and precise determination of NO₂ exposures. A concentration-dependent conversion factor is required in calculations and the molecular sieve solid sorbent must be water-washed before impregnation and tube packing.

11. References

- 11.1. **Occupational Safety and Health Administration Technical Center:** *Nitrogen Dioxide in Workplace Atmospheres (Ion Chromatography)*, by J.C. Ku (USDOL/OSHA-SLTC Method No. ID-182). Salt Lake City, UT. Revised 1991.
- 11.2. **Saltzman, B.E.:** Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere. *Anal. Chem.* 26:1949 (1954).
- 11.3. **Gold, A.:** Stoichiometry of Nitrogen Dioxide Determination in Triethanolamine Trapping Solution. *Anal. Chem.* 49:1448-50 (1977).
- 11.4. **Blacker, J.H.:** Triethanolamine for Collecting Nitrogen Dioxide in the TLV Range. *Am. Ind. Hyg. Assoc. J.* 34:390 (1973).
- 11.5. **Vinjamoori, D.V. and Chaur-Sun Ling:** Personal Monitoring Method for Nitrogen Dioxide and Sulfur Dioxide with Solid Sorbent Sampling and Ion Chromatographic Determination. *Anal. Chem.* 53:1689-1691 (1981).
- 11.6. **Occupational Safety and Health Administration Analytical Laboratory:** Precision and Accuracy Data Protocol for Laboratory Validations. In *OSHA Analytical Methods Manual*. Cincinnati, OH: American Conference of Governmental Industrial Hygienists (Pub. No. ISBN: 0-936712-66-X), 1985.
- 11.7. **National Institute for Occupational Safety and Health:** *Documentation of the NIOSH Validation Tests* by D. Taylor, (DHEW/NIOSH Pub. No. 77-185). Cincinnati, OH, 1977.
- 11.8. **Mandel, J.** In *Treatise on Analytic Chemistry*. 2nd ed. Kolthoff, I.M. and Elving, P.J., ed. New York: John Wiley and Sons, Inc., 1978. p 282.
- 11.9. **Occupational Safety and Health Administration Analytical Laboratory:** *OSHA Analytical Methods Manual* (USDOL/OSHA-SLTC Method No. ID-109). Cincinnati, OH: American Conference of Governmental Industrial Hygienists (Pub. No. ISBN: 0-936712-66-X), 1985.
- 11.10. **Dixon, W.J. and F.J. Massey, Jr.:** *Introduction to Statistical Analysis*. 2nd ed. New York: McGraw-Hill Book Co., 1957. pp 289-292.
- 11.11. **Analytical Methods Committee:** Recommendations for the Definition, Estimation and Use of the Detection Limit. *Analyst* **112(2)**:199-204 (1987).
- 11.12. **Morgan, G.B., C. Golden, and E.C. Tabor:** "New and Improved Procedures for Gas Sampling and Analysis in the National Air Sampling Network" Paper presented at the 59th Annual Meeting of the Air Pollution Control Association, San Francisco, CA, 1966.

- 11.13. **National Institute for Occupational Safety and Health:** *NIOSH Manual of Analytical Methods* by D. Taylor, (DHEW/NIOSH Pub. No. 78-175). Cincinnati, OH, 1978. Method no. S320.
- 11.14. **Occupational Safety and Health Administration Technical Center:** *Nitric Oxide Backup Data Report (ID-190)* by J.C. Ku. Salt Lake City, UT. Revised 1991.

Table 1
Analysis* Nitrogen Dioxide

Level**	0.5 × PEL			1 × PEL			2 × PEL		
	µg taken	µg found	DE	µg taken	µg found	DE	µg taken	µg found	DE
	12.35	12.50	1.01	23.78	24.38	1.03	58.36	60.68	1.04
	15.48	16.35	1.06	29.82	24.12	***	53.06	54.42	1.03
	12.59	13.11	1.04	27.44	29.31	1.07	52.14	54.95	1.05
	15.72	16.80	1.07	25.25	27.00	1.07	65.68	68.36	1.04
	13.26	13.90	1.05	24.88	26.33	1.06	57.08	61.73	1.08
	12.28	13.10	1.07	31.10	33.36	1.07	52.33	54.91	1.05
	12.08	12.55	1.04						
	14.97	16.46	1.10						
N			8			5			6
Mean			1.06			1.06			1.05
Std Dev			0.027			0.017			0.017
CV1			0.025			0.016			0.016

CV1 (pooled) = 0.021

Ave. DE = 1.06

DE = Desorption efficiency

*SKC tubes, lot no. 374, were used

**Transitional PEL of 5 ppm NO₂ was used

***Excluded from statistical analysis as an outlier

Table 2
 Sampling and Analysis* Nitrogen Dioxide

Test Level**	Found µg	Air Vol (L)	Found ppm	Taken ppm	Recovery (in %)
<u>0.5 × PEL</u>	14.46	2.59	2.97	2.64	113
	12.32	2.23	2.94	2.64	111
	10.59	1.94	2.90	2.64	110
	14.37	2.62	2.92	2.64	111
	16.03	2.81	3.03	2.64	115
	15.02	2.67	2.99	2.64	113
			N		6
			Mean		112
			Std Dev		1.8
			CV2		0.016
<u>1 × PEL</u>	28.77	2.59	5.90	5.06	117
	23.61	2.23	5.63	5.06	111
	21.01	1.94	5.76	5.06	114
	27.59	2.62	5.60	5.06	111
	28.24	2.81	5.34	5.06	106
	29.17	2.67	5.81	5.06	115
			N		6
			Mean		112
			Std Dev		3.9
			CV2		0.035
<u>2 × PEL</u>	56.83	2.59	11.66	9.45	123
	46.99	2.23	11.20	9.45	119
	38.21	1.94	10.47	9.45	111
	53.06	2.62	10.76	9.45	114
	55.53	2.81	10.50	9.45	111
	54.39	2.67	10.83	9.45	115
			N		6
			Mean		115
			Std Dev		4.8
			CV2		0.042

CV2 (pooled) = 0.033 CVT (pooled) = 0.034
 Ave. Recovery = 113% Overall Error = ±19.8%

*SKC tubes, lot no. 306, were used
 **Transitional PEL of 5 ppm NO₂ was used

Table 3
Collection Efficiency (25 °C and 50% RH)

Sample No.	µg NO ₂ Found		% Collection Efficiency
	First Section	Second Section	
1	56.83	2.32	96.1
2	46.99	ND	100.0
3	38.21	ND	100.0
4	53.06	2.19	96.0
5	55.53	1.98	96.6
6	54.39	2.30	95.9
		Average	97.4

- Note: (1) SKC tubes, lot no. 306, were used
- (2) Sampling rate = 0.2 L/min
Sampling time = 15 min
- (3) Concentration = approximately 2 times OSHA Transitional PEL
- (4) ND = None detectable < 0.24 µg NO₂⁻ (3-mL sample volume)

Breakthrough Study (25 °C and 30% RH)

Sample No.	µg NO ₂ Found		% Breakthrough
	1st Tube	2nd Tube	
1	103.8	3.34	3.1
2	104.5	ND	0
3	105.1	3.31	3.1
4	103.2	ND	0
		Average	1.6

- Note: (1) 1st and 2nd tube = SKC tubes, lot no. 374, were used
- (2) Sampling rate = 0.175 L/min
Sampling time = 15 min
- (3) Generation concentration = 21 ppm NO₂
- (4) ND = None detectable < 0.24 µg NO₂⁻ (3-mL sample volume)

Table 4
Storage Stability Test* Nitrogen Dioxide

Storage Day	Found µg	Air Vol(L)	Found ppm	Taken ppm	Recovery (%)
<u>Day 1</u>	28.77	2.59	5.90	5.06	117
	23.61	2.23	5.63	5.06	111
	21.01	1.94	5.76	5.06	114
	27.59	2.62	5.60	5.06	111
	28.24	2.81	5.34	5.06	106
	29.17	2.67	5.81	5.06	115
			N	6	
			Mean	112	
			Std Dev	3.9	
			CV	0.035	
<u>Day 5</u>	25.74	2.61	5.24	5.04	104
	23.56	2.23	5.61	5.04	111
	20.69	1.93	5.70	5.04	113
	26.52	2.60	5.42	5.04	108
	29.32	2.72	5.73	5.04	114
	28.41	2.61	5.79	5.04	115
			N	6	
			Mean	111	
			Std Dev	4.2	
			CV	0.038	
<u>Day 15</u>	24.56	2.61	5.00	5.04	99.2
	22.64	2.23	5.40	5.04	107
	20.56	1.93	5.66	5.04	112
	28.27	2.60	5.78	5.04	115
	29.50	2.72	5.76	5.04	114
	28.69	2.61	5.84	5.04	116
			N	6	
			Mean	111	
			Std Dev	6.4	
			CV	0.058	
<u>Day 29</u>	27.34	2.61	5.57	5.04	111
	23.95	2.23	5.71	5.04	113
	23.66	1.93	6.52	5.04	129
	27.58	2.60	5.64	5.04	112
	28.41	2.72	5.55	5.04	110
	31.92	2.61	6.50	5.04	129
			N	6	
			Mean	117	
			Std Dev	9.2	
			CV	0.079	

* SKC tubes, lot no. 306 were used

Table 5
 Relative Humidity Test (25 °C)
 *Generated NO₂ Concentration = 2.64 ppm

RH, %	34	50	80
NO ₂ Found, ppm	2.74	2.79	2.88
	2.73	2.94	2.81
	2.65	2.90	2.79
	3.11	2.92	2.91
	2.73	3.03	3.10
	2.77	2.99	2.86
N	6	6	6
Mean, ppm	2.79	2.93	2.89
Std Dev, ppm	0.16	0.083	0.11
CV	0.058	0.028	0.038
Recovery	106%	111%	109%

F test results:

F_{calc} = 2.078,

F_{crit} = 6.36, p < 0.01

*SKC tubes, lot no. 374, were used

Table 6
Comparison of Methods*[Ion Chromatographic (IC) vs. Polarographic (DPP)]

0.5 × PEL**			1 × PEL**			2 × PEL**		
ppm Found			ppm Found			ppm Found		
IC	DPP	RR	IC	DPP	RR	IC	DPP	RR
3.41	3.17	1.076	5.93	5.55	1.068	10.11	10.11	1.000
3.43	3.19	1.075	6.21	6.03	1.030	10.20	10.39	0.982
3.57	3.27	1.092	6.21	5.91	1.051	10.73	10.23	1.049
3.40	3.19	1.066	5.95	5.61	1.061	10.33	10.09	1.024
3.46	3.33	1.039	5.88	5.58	1.054	10.11	10.03	1.008
3.39	2.82	***	6.15	6.00	1.025	11.96	10.49	1.140
N		5			6			6
Mean		1.070			1.048			1.034
Std Dev		0.020			0.017			0.057
CV		0.018			0.016			0.055

* SKC tubes, lot no. 374, were used

** Transitional PEL of 5 ppm NO₂ was used

*** Excluded from statistical analysis as an outlier

RR = Relative ratio, IC Found (ppm)/DPP Found (ppm)

Linear Regression Comparison (also see Figure 2)

Correlation coefficient (r) = 0.9938

Slope (b) = 1.0194

Intercept (a) = 0.1587

Std dev of slope (Sb) = 0.0295

Table 7
 Qualitative Detection Limit - Nitrogen Dioxide
 Rank Sum Test For n(s) = n(b) = 10

Rank	NO ₂ (as nitrite)					
	0.08 µg/mL Peak Area		0.16 µg/mL Peak Area		0.32 µg/mL Peak Area	
1	0.50	RBL	0.50	RBL	0.50	RBL
2	0.57	RBL	0.57	RBL	0.57	RBL
3	0.70	RBL	0.70	RBL	0.70	RBL
4	0.72	RBL	0.72	RBL	0.72	RBL
5	0.83	RBL	0.83	RBL	0.83	RBL
6	1.03	RBL	1.03	RBL	1.03	RBL
7	1.05	RBL	1.05	RBL	1.05	RBL
8	1.13	RBL	1.13	RBL	1.13	RBL
9	1.13	RBL	1.13	RBL	1.13	RBL
10	1.16	RBL	1.16	RBL	1.16	RBL
11	1.86	STD	2.14	STD	4.02	STD
12	1.89	STD	2.29	STD	4.15	STD
13	1.89	STD	2.41	STD	4.33	STD
14	1.89	STD	2.46	STD	4.49	STD
15	1.93	STD	2.58	STD	4.61	STD
16	1.99	STD	2.77	STD	4.64	STD
17	2.10	STD	2.79	STD	4.67	STD
18	2.10	STD	2.83	STD	4.78	STD
19	2.16	STD	2.90	STD	4.81	STD
20	2.18	STD	2.93	STD	4.96	STD
Rb =	55		55		55	
C =	99.9%		99.9%		99.9%	

Qualitative detection limit for nitrogen dioxide = 0.08 µg/mL or 0.24 µg (3-mL sample volume).
 This corresponds to a concentration of 0.07 ppm NO₂ for a 3-L air volume.

Note: (1) RBL = Reagent Blank
 (2) STD = Standard
 (3) Peak Area = measured peak area/100,000

Table 7 (Cont.)
Quantitative Detection Limit - Nitrogen Dioxide (as NO₂)

Sample No.	Blank Peak Area	0.08 µg/mL Peak Area	0.16 µg/mL Peak Area	0.32 µg/mL Peak Area
1	0.50	1.86	2.14	4.02
2	0.57	1.89	2.29	4.15
3	0.70	1.89	2.41	4.33
4	0.72	1.89	2.46	4.49
5	0.83	1.93	2.58	4.61
6	1.03	1.99	2.77	4.64
7	1.05	2.10	2.79	4.67
8	1.13	2.10	2.83	4.78
9	1.13	2.16	2.90	4.81
10	1.16	2.18	2.93	4.98
N	10	10	10	10
Mean	0.88	2.00	2.61	4.55
Std Dev	0.25	0.12	0.27	0.30
CV	0.282	0.062	0.105	0.067

Peak Area = measured peak area/100,000

The quantitative detection limit is calculated using the equation:

$$C_{ld} = k(sd)/m \qquad C_{ld} = 10(0.248)/10.83 = 0.23 \mu\text{g/mL}$$

where:

- C_{ld} = the smallest reliable detectable concentration an analytical instrument can determine at a given confidence level
- k = 10, thus giving confidence that any detectable signal will be greater than or equal to an average blank reading plus ten times the standard deviation (area reading > Blave + 10sd)
- sd = standard deviation of blank readings
- m = analytical sensitivity or slope as calculated by linear regression

Quantitative detection limit = 0.23 µg/mL (as nitrite) or 0.69 µg (3-mL sample volume). This corresponds to 0.19 ppm NO₂ for a 3-L air volume.

Table 8
Nitrogen Dioxide Conversion factor

NO ₂ ppm	Samples	Std Dev	CV	Mean*
12.89	7	0.038	0.074	0.519
25.20	7	0.037	0.070	0.533
49.79	6	0.022	0.043	0.517
97.90	6	0.020	0.044	0.450
192.57	7	0.025	0.068	0.368

* Average conversion factor. This was calculated from sample results and assumed a 100% recovery.

Table 9
 Sampling and Analysis (Supelco Tubes)* Nitrogen Dioxide

Test Level**	Found µg	Air Vol (L)	Found ppm	Taken ppm	Statistics
<u>0.5 × PEL</u>	5.80	2.19	1.41	2.62	
	6.25	1.90	1.75	2.62	
	7.71	1.71	2.40	2.62	
	8.52	2.24	2.02	2.62	
	5.06	2.40	1.12	2.62	
	8.71	2.56	1.81	2.62	
				N	6
				Mean	66.9%
				Std Dev	17.0
				CV	0.26
<u>1 × PEL</u>	15.91	2.19	3.86	5.08	
	12.73	1.90	3.56	5.08	
	11.45	1.71	3.56	5.08	
	15.82	2.24	3.75	5.08	
	16.27	2.40	3.60	5.08	
	18.94	2.56	3.93	5.08	
				N	6
				Mean	73.0%
				Std Dev	3.2%
				CV	0.043
<u>2 × PEL</u>	30.11	2.19	7.31	9.66	
	22.77	1.90	6.35	9.66	
	22.48	1.71	6.99	9.66	
	28.63	2.24	6.79	9.66	
	31.14	2.40	6.90	9.66	
	34.04	2.56	7.07	9.66	
				N	6
				Mean	71.4%
				Std Dev	3.3%
				CV	0.047

* Supelco tubes, Lot No. 582-99, were used

**Transitional PEL of 5 ppm NO₂ was used

CV(pooled) = 0.15 Ave. Recovery = 70.4% Overall Error = ±59.6%

A block diagram of the major components of the dynamic generation system is shown below. The system consists of four essential elements, a flow, temperature and humidity control system, a nitrogen dioxide vapor generating system, a mixing chamber and an active sampling manifold.

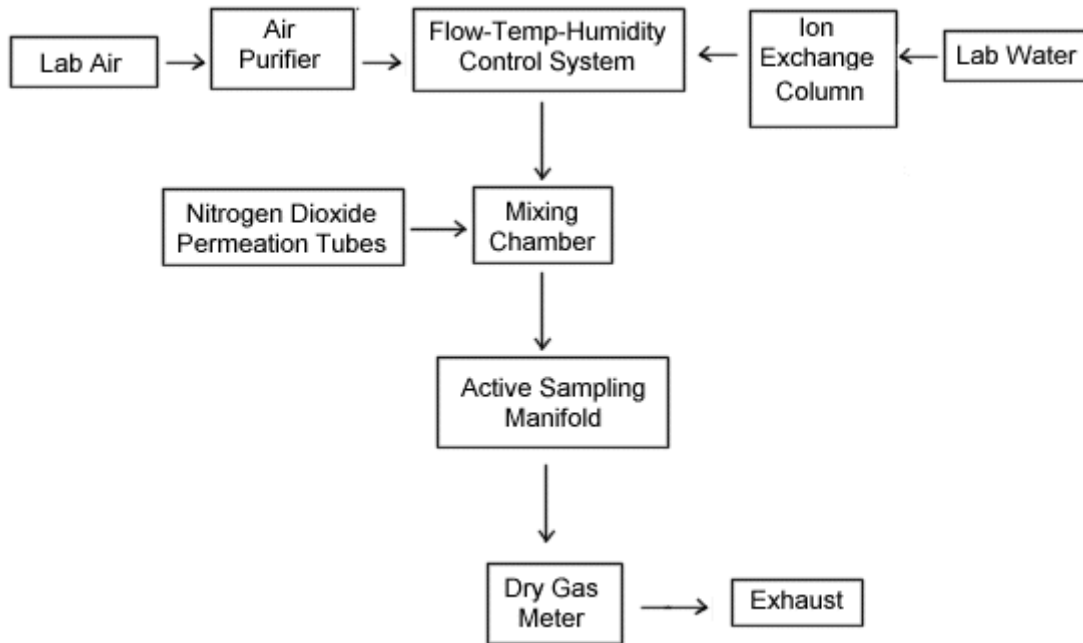
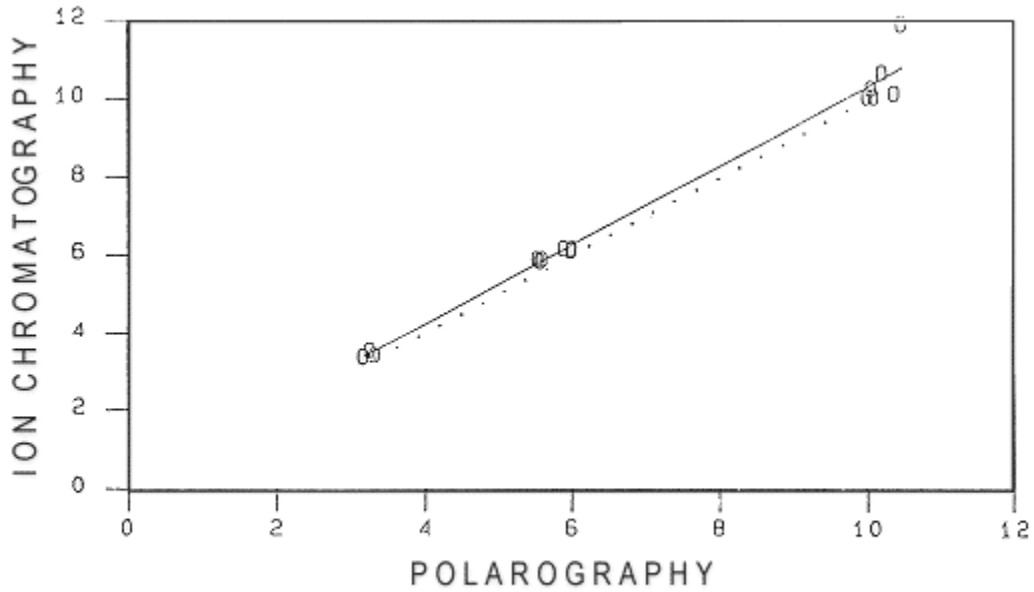


Figure 1

Linear Regression Comparison Ion Chromatographic vs. Polarographic Analysis of Nitrogen Dioxide



COORDINATES ARE PPM NITROGEN DIOXIDE FOUND

Dotted Line = Ideal Agreement Between Methods

Solid Line = Found Agreement Between Methods

Figure 2

Detection Limit

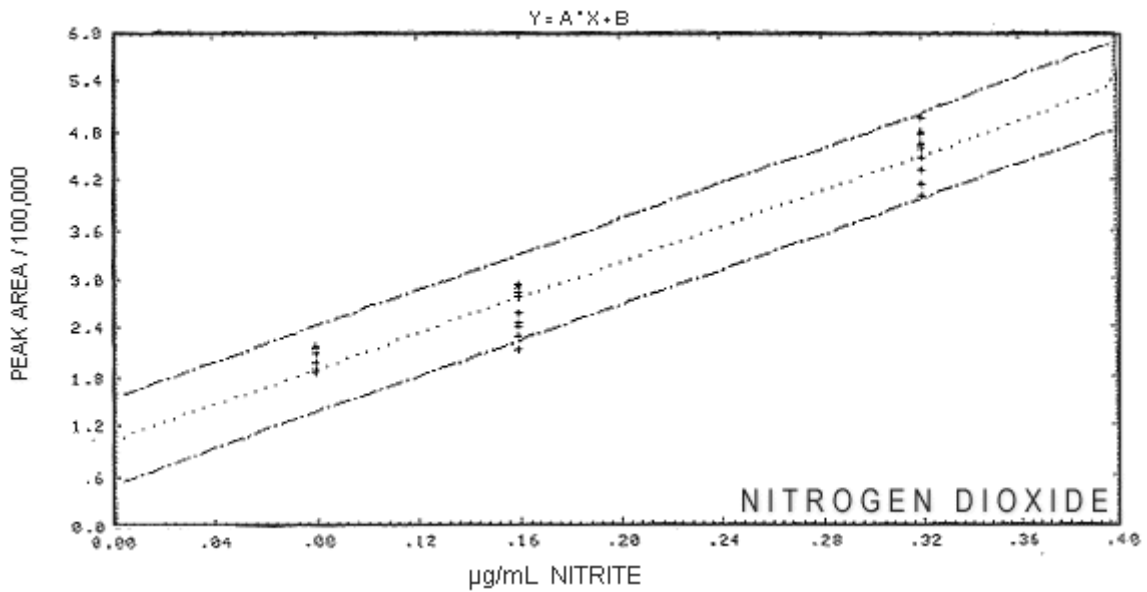


Figure 3