



Method no.:	ID-190
Matrix:	Air
OSHA Permissible Exposure Limit:	25 ppm
Collection Device:	The sampling device consists of: 1) Two glass tubes which contain triethanolamine-impregnated molecular sieve, 2) A middle tube which contains an oxidizer and 3) A personal sampling pump is used to draw a measured volume of air through the tubes.
Recommended sampling rate:	0.025 L/min
Recommended maximum air volume:	6.0 L
Analytical procedure:	The sample is desorbed using a 1.5% triethanolamine solution and analyzed as nitrite by ion chromatography.
Detection limit:	
Qualitative:	0.11 ppm (6-L air sample)
Quantitative:	0.32 ppm (6-L air sample)
Precision and accuracy	
evaluation range:	13.0 to 50.5 ppm
CV _T :	0.082
Bias:	+3.3%
Overall error:	±19.7%
Method classification:	Validated method
Chemist:	James Ku
Date (Date revised):	April 1989 (May 1991)

Branch of Inorganic Development
OSHA Technical Center
Salt Lake City, Utah

Commercial manufactures 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 nitric oxide (NO). Samples are taken in the breathing zone of workplace personnel and analyses are performed by ion chromatography (IC).

1.1. History

Previous methods involved oxidation of NO to nitrogen dioxide (NO₂) using a chromate compound and subsequent conversion of NO₂ to nitrite using triethanolamine-impregnated molecular sieve (TEA-IMS) sampling tubes. Common methods used a combination sampling tube and NO was determined colorimetrically (as NO₂⁻) using a modified Griess-Saltman reaction (8.1-8.2). This method, like most colorimetric procedures, can have significant interferences.

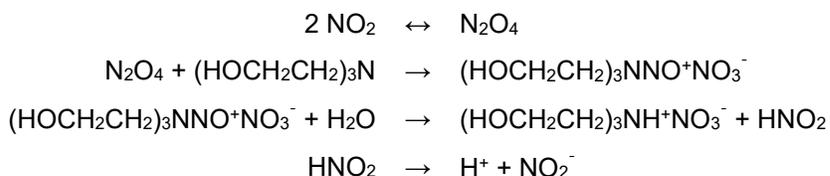
A differential pulse polarographic (DPP) method (8.3) was later developed to improve analytical sensitivity and decrease the potential for interferences. The sensitivity of the DPP method was more than adequate for measuring workplace concentrations of NO; however, the nitrite ion is unstable in the pH range (pH 1-2) used during analysis (8.4).

Method no. ID-190 uses the TEA-IMS sampling tube/chromate oxidizer approach. Samples are analyzed by IC.

1.2. Principle

A known volume of air is drawn through the sampling device which captures any nitrogen dioxide (NO₂) in the sampled air and also converts any NO to nitrite ion (NO₂⁻). The sampling device consists of three glass tubes connected in series. The front and back tubes contain TEA-IMS, the middle or oxidizer tube contains an inert carrier impregnated with a chromate salt. The first TEA-IMS tube does not capture NO; this tube is only used to capture and convert to NO₂⁻ any NO₂ present in the sampled air. The middle tube oxidizes the sampled NO to NO₂. The back TEA-IMS tube then captures and convert this NO₂ to NO₂⁻. Both TEA-IMS samples are desorbed using an aqueous triethanolamine (TEA) solution and analyzed as NO₂⁻ by IC. The front tube analytical results are reported as NO₂ and the back tube as NO.

The conversion mechanism of NO₂ gas to NO₂⁻ has been proposed by Gold (8.5). The following is Gold's proposal for the reaction of equivalent amounts of NO₂ and TEA in an aqueous solution:



Nitrogen dioxide disproportionates to NO₂⁻ and nitrate (NO₃⁻) in the presence of TEA and water. The NO₂⁻ formed from the above reaction can be analyzed via conventional analytical methods (8.1-8.4, 8.6-8.7) including IC. Unfortunately NO₂⁻ is found in commercial TEA-IMS sorbent as a

significant contaminant. This contaminant ruled out further research to also measure 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 stoichiometric factor of 0.5 is seen only when NO₂ concentrations are greater than 10 ppm (8.1-8.3, 8.5-8.9). The deviation from ideal stoichiometry is believed to be due to competing reactions; however, evidence to support a competing mechanism has not been found (8.5).

1.3. Advantages and disadvantages

- 1.3.1. This method has adequate sensitivity for determining compliance with OSHA Time Weighted Average (TWA) Permissible Exposure Limits (PEL) for workplace exposures to NO.
- 1.3.2. The sampling device can be used to simultaneously collect NO and NO₂; however, results for NO₂ may not reflect short-term exposures (see Section 5.2 for more details).
- 1.3.3. The analysis is simple, rapid, easily automated and is specific for NO₂⁻.
- 1.3.4. After analytical sample preparation, NO exposures (as nitrite ion) can also be determined by colorimetric or polarographic analytical techniques (8.1-8.3).
- 1.3.5. 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 (DI H₂O) to remove any soluble chloride salts.
- 1.3.6. Another disadvantage is the need for a concentration-dependent conversion factor when calculating results.

1.4. Physical properties (8.10, 8.11)

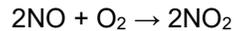
Nitric oxide (CAS no. 10102-43-9), one of several oxides of nitrogen, is a colorless gas. A deep blue color is usually noted when NO is in the liquid state and a blueish-white color when solid. Other physical characteristics of NO are:

formula weight:	30.005
specific gravity:	1.27 at -150.2 °C (as liquid)
melting point:	-163.6 °C
boiling point:	-151.8 °C
vapor pressure:	1.04 (air=1)
solubility:	4.6 mL NO in 100 mL H ₂ O
synonyms:	mononitrogen monoxide; nitrogen monoxide (nitrogen monoxide has also been used as a synonym for nitrous oxide (N ₂ O))

1.5. Some industrial sources for potential nitric oxide exposures are:

agricultural silos	nitric acid production
arc or gas welding (confined space)	nitrogen fertilizer production
electroplating plants	nitro-explosive production
food and textile bleaching	nitrosyl halide production
jewelry manufacturing	pickling plants
metal nitrosyl carbonyl production	

Nitrogen dioxide and nitric oxide usually exist together in industrial settings. Nitric oxide is reactive in air and produces the following equations (8.10):



$$d(\text{NO}_2)/dt = K(\text{O}_2)(\text{NO})^2$$

(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 operations is shown (8.10):

<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 (8.11-8.14)

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

1.6.1. Nitric oxide is classified as a respiratory irritant. The main route of exposure is inhalation; however, physiological damage can occur from exposures to the eyes or skin.

The term "silo-fillers' disease" has been used to describe exposure to nitric as well as other nitrogen oxides. The national population-at-risk for exposure to nitrogen oxides has been estimated by NIOSH to be approximately 950,000 employees (National Occupational Hazard Survey, 1972-74). When encountering either NO or NO₂ at high concentrations, both species will usually be present. Little scientific data is available regarding exposures to NO only. The majority of collected data concerns exposure to NO₂ because NO appears to be only one-fifth as toxic as NO₂ at low concentrations.

Symptoms immediately following NO exposure are usually mild or not apparent. Severe symptoms may not appear up to 72 hours after exposure.

1.6.2. Mild exposure to NO can result in symptoms such as:

cough	shortness of breath
painful breathing	chest pain
increased breathing rate	weakness
methemoglobinemia	

More severe exposures (>100 ppm) are characterized by pulmonary edema, cyanosis, pneumonia, severe methemoglobinemia, respiratory failure, and death.

1.6.3. The IDLH (Immediately Dangerous to Life or Health) concentration is 100 ppm NO. The LCLo (Lethal Concentration - Low) for inhalation by mice is 320 ppm.

1.6.4. Mechanism for toxicity:

Nitric oxide is slightly soluble in water and forms nitrous and nitric acid. This reaction occurs with lung tissue and produces respiratory irritation and edema. Alkali present in the lung tissue neutralizes the nitrous and nitric acids to nitrite and nitrate salts which are then absorbed into the bloodstream. The end result is the formation of nitroso-hemoglobin complexes and methemoglobin in the circulatory system.

The formation of hemoglobin complexes is thought to contribute to the toxicity of NO but is not considered to be the sole source of the toxic reaction. The respiratory damage from nitrous and nitric acid appears to be more significant.

2. Range, Detection Limit and Sensitivity

The analytical parameters and limits of this method have been previously described (8.8). Brief descriptions are in Section 3 below.

3. Method Performance

This method was evaluated in the concentration range of 13.0 to 50.5 ppm. Air volumes of approximately 6 L and flow rates of about 0.025 L/min were used. Samples were collected for 240 min. Sample results were calculated using the concentration-dependent conversion factors mentioned in Section 7. Listed on the cover page (CV_T, bias overall error) and below are evaluation data taken from the backup report (8.9).

Qualitative detection limit ¹ :	0.08 µg/mL (as NO ₂ ⁻) 0.11 ppm NO (6 L air volume)
Quantitative detection limit ¹ :	0.23 µg/mL (as NO ₂ ⁻) 0.32 ppm NO (6 L air volume)
Sensitivity (1 to 3 µg/mL nitrite)	
Hewlett-Packard ² :	239,000 area counts per 1 µg/mL NO ₂ ⁻
Dionex ² :	10,000 area counts per 1 µg/mL NO ₂ ⁻
Collection efficiency ³ :	100%
Breakthrough:	none at levels tested ³
Sample storage	at least 30 days (20-25 °C)

¹ Detector setting = 3 microsiemens, sample loop = 50 µL (8.8)

² A model 3357 data reduction system (Hewlett-Packard, Avondale, PA) (1 area unit = 0.25 microvolt-second) was used during first part of evaluation. An Autolon 400 data reduction system (Dionex, Sunnyvale, CA) was used for later analyses.

³ Collection efficiency samples were taken using a concentration of 50.5 ppm NO for 240 min, 50% RH, and a flow rate of 0.025 L/min. Breakthrough tests were performed at 25 °C, 50% RH, and a flow rate of 0.025 L/min. Samples were collected at a concentration of 200 ppm for 60, 120, 180, and 240 min.

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 samples.
- 4.2. Any compound that has 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, column characteristics, and/or pump flow rate.
- 4.4. If there is an unresolvable interference, alternate polarographic or colorimetric methods may be used (8.1-8.3).
- 4.5. Contaminant anions normally found in molecular sieve, such as NO₂⁻, SO₄²⁻, and PO₄³⁻, do not interfere. Large amounts (greater than 4 to 5 µg/mL) of Cl⁻ can interfere.

5. Sampling

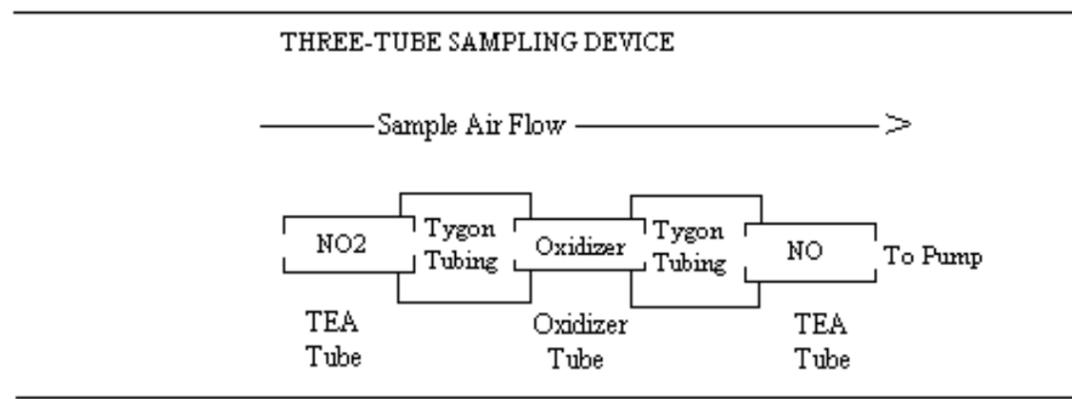
5.1. Equipment

- 5.1.1. A three tube sampling device is commercially available (NO/NO₂ sampling tubes, cat no. 226-40, water-washed, SKC, Inc, Eighty Four, PA) and can be used to simultaneously sample NO₂ and NO, or sample for only NO₂. This device consists of three flame-sealed glass tubes:

- 1) Nitrogen dioxide is collected in the first tube which contains 400 mg TEA-IMS.
- 2) The second (oxidizer) tube converts NO to NO₂ and contains approximately 1 g of a chromate compound impregnated on an inert carrier.
- 3) The last 400 mg TEA-IMS packed tube collects the converted NO₂.

All molecular sieve used for tube packing must be washed with DI H₂O before impregnation with TEA. 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 treated glass wool is placed in the front and rear of each tube. 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, NO₂ and NO can be collected simultaneously. The first TEA-IMS tube must be in place to prevent the collection of NO₂ by the second TEA-IMS tube.



5.1.2. Personal sampling pumps capable of sampling at a flow rate of approximately 0.025 L/min are used.

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

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 exposure limits [the NO₂ PEL is 5 ppm Ceiling value (8.15). Nitric oxide is a TWA PEL.] and flow rates dictates a need for a separate assessment of NO₂. Nitric oxide is collected at a 0.025 L/min pump flow rate; however, a longer sampling time will be necessary to collect a detectable amount of NO₂ than for a short-term measurement. Concentrations NO₂ may vary in the workplace during a longer sampling period.

- 5.2.1. Calibrate the sampling pumps to a flow rate of 0.025 L/min.
- 5.2.2. Connect the sampling device to a pump. The different sampling schemes are listed:
 - a) Sampling for NO₂ only: Use a single TEA-IMS tube (8.8).
 - b) Sampling for both NO and NO₂: The three-tube device is used. The sampling device must be assembled as shown above. Label the first tube "NO₂". Label the tube following the oxidizer section is labeled "NO".
- 5.2.3. Place the sampling tube or device in the breathing zone of the employee.
- 5.2.4. Collect the sample at the listed flow rates and sampling times:
 - a) For NO₂ only: 0.200 L/min for at least 15 min (8.8).
 - b) For both NO and NO₂: 0.025 L/min for 4 h per sample. (Note: The front tube of the three-tube device can be submitted for NO₂ analysis; however, analytical results may not represent short-term exposures.)
- 5.2.5. The maximum recommended air volume is 6 L per NO sample. Take enough samples for NO to cover the work shift.

Note: One oxidizer tube per sample is sufficient for concentration ranges of NO usually encountered in industrial settings. A color change from orange to blue-green will be noticed if the oxidizer is depleted.

6. Analysis

6.1. Precautions

- 6.1.1. Refer to instrument and standard operating procedure (SOP) (8.16) 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 eyewear, gloves and lab coat 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 0.5 mL sample vials.
- 6.2.3. Laboratory automation system: Ion chromatograph interfaced to a data reduction and control system (Autolon 400 or 450 System, Dionex).
- 6.2.4. Micromembrane suppressor, anion (Model AMMS-1, Dionex).
- 6.2.5. Separator and guard columns, anion (Model HPIC-AS4A and AG4A, Dionex).
- 6.2.6. Disposable syringes (1 mL) and 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.

- 6.2.7. Erlenmeyer flasks, 25-mL, or scintillation vials, 20-mL.
- 6.2.8. Miscellaneous volumetric glassware: Micropipettes, volumetric flasks, graduated cylinders, and beakers.
- 6.2.9. 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 1.50 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	*
30	100	3
50	100	5

* 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

- 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 (8.16). 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.

Chromatogram of a 25 ppm Nitric Oxide Sample (HPIC-AS4A Column)

Peak Num	Ret Time	Peak Name	Area	Height
1	0.90		2.412e+004	3798
2	1.18	chloride	7.132e+004	7902
3	1.65	chloride	2.975e+004	1901
4	2.02	nitrite	1.647e+005	19984
5	3.67	nitrite	4.857e+004	4138
6	4.77		5.744e+003	376
7	6.48		3.990e+003	232

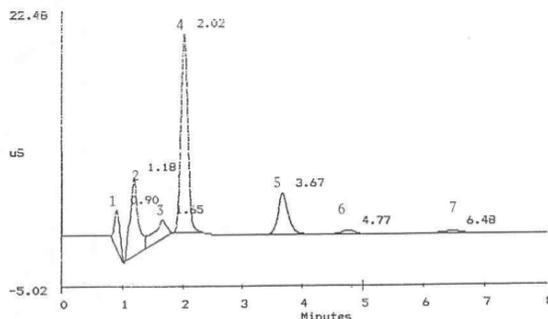


Figure 1. Chromatogram of nitric oxide.

- 7.2. Prepare a concentration-response curve by plotting the concentration of the standards in $\mu\text{g/mL}$ (or $\mu\text{g/sample}$ if the same solution volumes are used for samples and standards) versus peak areas or peak heights. Calculate sample concentrations from the curve and blank correct all samples.
- 7.3. The concentration of NO in each air sample is expressed in ppm and is calculated as:

$$\text{ppm NO} = \frac{\text{Molar Volume} \times \mu\text{g/mL NO}_2^- \times \text{Solution Volume} \times \text{Conversion} \times \text{GF}}{\text{Formula Weight} \times \text{Air Volume}}$$

where:

Molar volume = 24.46 (25 °C and 760 mmHg)

$\mu\text{g/mL NO}_2^-$ = blank corrected sample result

Conversion = varies with concentration

GF (gravimetric factor NO/NO₂) = 0.6522

Formula weight (NO₂) = 30.005

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

Below 10 ppm NO

From 0 to 10 ppm, the average relationship has been experimentally determined to be (8.1-8.3, 8.5-8.9):

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

or conversely:

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

Simplifying the equation and calculating the ppm using a 10-mL sample volume gives:

$$\text{ppm NO} = \frac{\mu\text{g/mL NO}_2^- \times 10 \text{ mL} \times 0.843}{\text{Air Volume (L)}}$$

Above 10 ppm NO

Above 10 ppm NO, the expected stoichiometric factor of 0.5 mole of nitrite to 1 mole of nitrogen dioxide gas is seen (8.5, 8.8-8.9). Therefore, the following calculation should be used for sample results above 10 ppm and a 10-mL sample volume:

$$\text{ppm NO} = \frac{\mu\text{g/mL NO}_2^- \times 10 \text{ mL} \times 1.0633}{\text{Air Volume (L)}}$$

7.4. Reporting Results

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

8. References

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Introduction

The procedure for the air sample collection and analysis of nitric oxide (NO) is described in OSHA Method No. ID-190 (11.1.). The NO sample is collected using a three-tube sampling device.

This method has been evaluated near the OSHA Transitional Permissible Exposure Limit (PEL) for 240-min samples. At the time of this study, the Time Weighted Average (TWA) PEL for NO is 25 ppm. The Final Rule PEL is also 25 ppm as a TWA.

Test atmospheres were generated and samples were collected and analyzed according to the procedures listed below.

Generation System

All generations of NO test atmospheres, and hence all experiments, with two exceptions, were performed using the apparatus shown in Figure 1. The analysis (Section 1) and detection limit experiments did not use a test atmosphere generation for sample preparation. Instead, samples were spiked with solutions of sodium nitrite. For further details regarding the detection limit experiment, see reference 11.2.

A cylinder of NO in nitrogen (1.05% NO, Air Products and Chemicals, Long Beach, CA) was used as the contaminant source. The NO was mixed, using a glass mixing chamber, with filtered, tempered air. A flow, temperature, and humidity control system (Miller-Nelson Research Inc., Model HCS-301) was used to condition the diluent air for mixing. 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.

Sample Collection

Air samples were collected from the Teflon manifold using calibrated SKC Model 222-3-10 low-flow pumps (approximately 0.025 L/min flow rate) during all generation experiments. Two different TEA-IMS sampling devices were commercially available for NO sampling at the beginning of the validation. The two devices listed below are designed to simultaneously collect NO₂ and NO. Preliminary studies indicated the SKC collection device (1) was the most suitable for collection of NO and NO₂:

1. SKC NO₂-NO collection device (SKC Cat. No. 226-40, water-washed): The sampling device consists of three separate glass tubes. A description of the tubes is given in reference 11.1. The SKC tubes used for all validation experiments were from lot no. 374 except for the storage stability experiment where lot no. 444 tubes were used.
2. Supelco combination tube: This combination tube contains all three sections in a single tube. Two 400-mg sections of TEA-IMS are separated by an oxidizer section. The Supelco tube uses a smaller mesh size of molecular sieve and only approximately 800 mg of oxidizer. Tubes from lot no. 564-07 were only used for a preliminary sampling and analysis experiment. Due to the low recoveries found during this preliminary study, further experiments using the Supelco combination tube were not performed.

Sample analysis

Note: The analytical portion of the method for NO is the same as the NO₂ method; both analyses are performed by determining the amount of NO₂⁻ produced from the NO₂-TEA reaction.

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, a conversion factor (C.F.) of 0.72 was first reported (11.3.). Later experiments indicated an average C.F. of 0.63 (11.2., 11.4.-11.5.). The 0.63 C.F. was used for all experiments in this evaluation which were conducted with concentrations less than 10 ppm NO. A C.F. of 0.5 was used for concentrations above 10 ppm NO.

Sample Results

Results were calculated using peak areas and linear regression concentration-response curves. A statistical protocol (11.6.) was used to evaluate results. Any calculation of error follows the general formula:

$$\text{Error}_i = \pm [|\text{mean bias}_i| + 2\text{CV}_i] \times 100\% \quad (95\% \text{ confidence})$$

where i is the respective sample pool being examined

Data were subjected to the Bartlett's test (11.7.) and a test for outliers (11.8.) to determine homogeneity of variance and identify any outliers. Both tests were conducted using the 99% confidence level.

Validation

The following experiments were conducted for the validation of Method No. ID-190:

1. Analysis - Desorption efficiency (DE) of spiked samples
2. Sampling and Analysis - generation and analysis of NO samples
3. Collection efficiency
4. Breakthrough tests.
5. Storage stability.
6. Sampling at different humidities.
7. Determination of the conversion factor for NO concentrations of 10 to 200 ppm.
8. Sampling and analysis of a mixture of NO and NO₂.

This analytical method was also compared to the polarographic method previously used by the OSHA laboratory. This method comparison and the detection limit determinations were performed during the NO₂ method validation (See reference 11.2. for more information). The quantitative detection limit was determined to be 0.08 µg/mL (as NO₂⁻).

A preliminary sampling and analysis experiment using Supelco tubes was also performed and is discussed in Section 9.

1. Analysis (Desorption Efficiency, DE)

Procedure: Eighteen spiked samples (6 samples at each test level) were prepared and analyzed. Samples were prepared by spiking known amounts of sodium nitrite solutions into TEA-IMS treated solid sorbent tubes. Calibrated micropipettes were used for spiking. The spiked concentrations corresponded to approximately 12.5, 25, and 50 ppm of NO when using a 0.025 L/min sampling rate for 240 min. These concentrations are approximately 0.5, 1, and 2 times the OSHA PEL.

Results: The results are listed in Table 1. Recoveries at these levels represent analytical DE. Results also provide recoveries, analytical error (AE), and extent of variability for the analytical portion of the method.

All analysis data passed the Bartlett's and outlier tests. Sample results were pooled. The analytical data for the method (Table 1) gave acceptable precision and accuracy (11.7.) and does not indicate a need for a desorption correction factor. The coefficient of variation for analysis (CV_1) was 0.045 and the average analytical recovery was 107.3%.

2. Sampling and Analysis

Procedure: A total of 20 samples were collected from dynamically generated test atmospheres and analyzed. The concentrations generated were about 0.5, 1, and 2 times the PEL. The generation system shown in Figure 1 was used. Samples were taken for 240 min at a RH and temperature of 50% and 25 °C, respectively.

Results: The results, as shown in Table 2, provide the overall error (OE) and precision of the sampling and analytical method. Overall error should be less than $\pm 25\%$ when calculated using the equation listed in the Introduction.

The Sampling and Analysis data show acceptable precision and accuracy (11.7.). All data passed both the outlier and Bartlett's test and the results were pooled. The coefficients of variation for spiked CV_1 (pooled) samples, generated CV_2 (pooled) samples and overall CV_T (pooled) are:

$$CV_1 \text{ (pooled)} = 0.045, \quad CV_2 \text{ (pooled)} = 0.080, \quad CV_T \text{ (pooled)} = 0.082$$

The sampling and analytical bias was +3.3%. Overall error was within guidelines ($< \pm 25\%$) and was $\pm 19.7\%$.

3. Collection Efficiency

Procedure: Dynamically generated samples were used to measure the sorbent collection efficiency at the upper concentration limit (50 ppm NO) of the validation. Six SKC sampling devices were connected to backup TEA-IMS tubes using Tygon tubing. This sampling train was configured using the following tube sequence:

1) TEA-IMS 2) oxidizer 3) TEA-IMS 4) TEA-IMS

This train was used to collect NO at 2 times the OSHA PEL for 240 min. A pump flow rate of approximately 0.025 L/min was used. The amount of NO collected in each TEA-IMS tube was measured.

Results: Results are reported in Table 3. The collection efficiency was calculated as:

$$\% \text{ Collection Efficiency} = \frac{\text{ug NO found in tube 3}}{\text{ug NO found in tube 3 + tube 4}} \times 100\%$$

Collection efficiency was 100% at 2 times the PEL, which indicates the sorbent media has adequate capacity for collecting NO within the validation range.

4. Breakthrough

Procedure: Test atmospheres were generated at a concentration greater than the validation level to determine if any breakthrough of NO occurs from the primary solid sorbent sampling tube (following the oxidizer) into a second tube. Breakthrough is considered significant if the concentration collected with the second tube is >5% of the results from the first tube. Twelve sampling devices were connected to backup tubes (as mentioned in Section 3.) and then to sampling pumps. All samples were collected at a concentration of 200 ppm and 0.025 L/min flow rate. Three sampling devices were removed from the generation system at 60, 120, 180, and 240 min. 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., 11.4.).

Results: Results are shown in Table 4. The extent of breakthrough was assessed by:

$$\% \text{ Breakthrough} = \frac{\text{ug NO found in tube 4}}{\text{ug NO found in tube 3 + tube 4}} \times 100\%$$

Breakthrough studies indicate the SKC sorbent tube and oxidizer capacity for NO is adequate for air concentrations up to 200 ppm when using air volumes and flow rates described. Further research to determine the actual breakthrough concentration was not conducted. It should be unlikely that industrial environments will exceed an exposure of eight times the PEL.

5. Storage Stability

Procedure: A study was conducted to determine if any storage problems existed for TEA-IMS tubes which had been used to collect samples. The procedure used is discussed below:

- 5.1. Twelve samples were collected at the OSHA PEL as described in the Introduction.
- 5.2. These samples were stored at 20 to 25 °C on a laboratory bench for the duration of the storage period.
- 5.3. Three samples were analyzed at 0, 5, 15, and 30 days.

Results: The results of the storage stability study are shown in Table 5. The mean of samples analyzed after 30 days was within ±5% of the mean of samples analyzed after 1 day. Samples may be stored in environmental conditions found in a laboratory setting for 30 days without a significant change in results.

6. Humidity Study

Procedure: A study was conducted to evaluate any effects on recovery when sampling at different humidities. Contaminant atmospheres conditioned at 30, 50, and 80% RH were generated at 25 °C. Six or seven SKC sampling devices were used at each RH level.

Results: Results are shown in Table 6. Data from sampling at different humidities displayed an apparent effect on sampling efficiency. As shown in Table 6, an analysis of variance (F test) was

performed on the data to determine if a significant difference in the results existed from changes in humidity. Sample recoveries and OE for the three different humidity levels were also considered. The calculated F value is greater than the critical value and a significant effect from humidity appears to exist. A slight decrease in average recovery is apparent at low humidity (30% RH); however, results are still within OE limits ($\pm 25\%$) and corrective action when sampling at low humidities appears unnecessary.

7. Conversion Factor (C.F.)

As described in OSHA Method No. ID-190 (11.1.), the proposed factor for the conversion of NO_2 gas to NO_2^- is concentration-dependent. If the reaction is stoichiometric, a C.F. of 0.5 would be seen experimentally; however, this does not appear to occur at low concentrations. For concentrations below 10 ppm, the average C.F. is 0.6 to 0.7 [as reported by Morgan et. al. (11.9.), in a previous OSHA study (11.10.), and by numerous others (11.3.-11.5.)]. For concentrations of 0 to 10 ppm NO_2 , a factor of 0.63 was adopted by OSHA (11.10.) and NIOSH (11.11.). The factor was not well defined at higher concentrations and needed further evaluation.

Procedure: The following two procedures were used to experimentally determine the C.F. for concentrations greater than 10 ppm.

7.1. Determination of C.F. using oxidation of NO

7.1.1. The same generation system shown in Figure 1 was used. Nitrogen dioxide was produced by flowing a diluted NO mixture through SKC oxidizer sections.

7.1.2. The generation system was set at 50% RH and 25 °C.

7.1.3. The NO_2 produced was then collected using impingers containing 1.5% TEA solutions. Variable time periods (30 to 360 min) and different concentration ranges were used. The TEA solutions were used in an attempt to avoid any extraneous background contribution or intrinsic contamination that is sometimes noted when using the impregnated solid sorbent. Samples were taken at a flow rate of about 0.025 L/min primarily to assure complete oxidation of the NO and secondarily to provide sufficient residence time of NO_2 in the TEA solutions.

7.2. Determination of C.F. using NO_2 permeation tubes

7.2.1. A second study was performed using permeation tubes (Thermedics Inc., Woburn, MA) as the NO_2 source. The system was setup as mentioned in reference 11.2.

7.2.2. The generation system was set at 50% RH and 25 °C.

7.2.3. Samples were taken using impingers containing 1.5% TEA. Flow rates of 0.15 mL/min were used to collect samples for 30 to 60 min (Note: A higher sample flow rate was possible because NO_2 was used instead of NO).

Results: The results for C.F. calculations from about 1 to 193 ppm are listed in Table 7. This data shows the C.F. for the 10 to 100 ppm concentration range averaged approximately 0.50; at about 200 ppm the factor apparently decreased to 0.37. Further work may be necessary to determine why the factor decreased at the 200 ppm level. As mentioned in Section 4, no breakthrough was found on backup tubes when sampling at 200 ppm.

Proposed curve fits for the C.F. are shown in Figure 2a and Figure 2b. Figure 2b is an expanded scale version of Figure 2a. As a comparison with other authors' experiments, some of the data (<15 ppm NO₂) used in the curve fit were taken from the following studies found in literature:

NO ₂ ppm	C.F.	Literature Source (reference no.)
0.01	1*	11.13., 11.14.
3.4	0.73	11.4., 11.5.
9.05	0.61	11.4., 11.5.
10.7	0.56	11.4., 11.5.

* The first data set (0.01, 1) is used to force a value of unity for a concentration well below the limit of detection. The C.F. value of unity was determined only for a passive monitor (11.13., 11.14.) where the NO₂ concentration at the monitor face is apparently very low (11.13.).

The conversion factor appears to follow either general curve fit:

$$Y = (a) \times (\text{NO})^b \quad (1)$$

or

$$Y = (a) + (b) \times \ln(\text{NO}) \quad (2)$$

where:

Y = calculated C.F.

NO = uncorrected ppm NO

a = slope; for equation (1), a = 0.7140, for (2), a = 0.7372

b = intercept; for equation (1), b = -0.09714, for (2), b = -0.06368

The standard deviation about the regression line (S_y/X) for (1) was 0.0536 and 0.0393 for equation (2).

According to the reaction proposed by Gold (11.4.), NO₂⁻ and triethanolammonium nitrate are formed in the reaction of NO₂ with TEA. The amount of nitrate (NO₃⁻) produced has not been documented at different NO₂ concentrations. As can be seen by Figure 2a and Figure 2b, as the concentration of NO₂ (or NO) decreases, the subsequent formation of NO₂⁻ (in relation to NO₂) increases. As the NO₂ concentration decreases, theoretically the NO₃⁻ concentration should also decrease. Although bubblers with TEA solutions were used at one point in the experiment in an attempt to rule out NO₃⁻ contamination, the NO₃⁻ concentrations could not be confirmed due to the apparent contamination of NO₃⁻ found in the generation system and sorbent material. The measured concentration of NO₃⁻ did not appear to change in relation to NO₂ concentration. Comparison of the ratios of peak areas for the two analytes (NO₂⁻/NO₃⁻) across the concentration range tested gave variable, almost random results. When considering NO₂ concentrations below 25 ppm, this ratio would be expected to increase as the concentration of NO₂ decreases.

The correction for the conversion of NO₂ to NO₂⁻ has been approximated using an average C.F. of 0.63 for less than 10 ppm NO (or NO₂) and 0.50 for concentrations above 10 ppm. A computer simulation using the approximate 0.63 and 0.5 C.F. values for a concentration range of 1 to 100 ppm gave results

within +11% of those calculated using equation (1). The approximate C.F.s were within +5% of the calculated factors for most of the concentration range. The greatest disagreement between calculated and approximate C.F.s occurs at about 10 ppm.

The two approximate C.F. values were used for all data contained in this backup report and were recommended in the method (11.1.). These two C.F. values appeared to be more convenient to use and the potential difference between calculated and approximate C.F. values in the concentration range tested is minor.

Further work to accumulate a larger data base of C.F. values and consequently more accurate slope and intercept values should be performed before extensive use of these equations (especially below 1 ppm NO₂). This work may also reveal whether one equation is more suitable to use. Also, a more controlled study of the NO₃⁻ concentration and contamination may shed light on the reaction mechanism at low concentrations.

8. Sampling and Analysis of a Mixture of NO and NO₂

Procedure: A determination of the ability of the three-tube sampling device to sample NO/NO₂ mixtures was assessed. A mixture of NO and NO₂ was generated using equipment described in the Introduction (for NO) and as mentioned in reference 11.2. (for NO₂). Samples were taken using the sampling device for 1 h at a flow rate of 0.15 L/min (50% RH and 25 °C).

Results: Results are shown in Table 8. The mixture study indicates the sampling tube is capable of collecting a mixture of NO and NO₂ at their respective PEL concentrations for 1 h.

9. Sampling and Analysis - Supelco Tubes

Procedure: A preliminary evaluation of the combination device 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. Two sets of six samples were taken at the PEL and 50% RH. A sampling flow rate of about 0.025 L/min and a sampling time of 4 h was used.

Results: Results are listed in Table 9. The Supelco tube results indicate extremely variable and mainly low recoveries when sampling at the PEL. The oxidizer in the Supelco tube contained only about 800 mg and may have contributed to the low recovery by not having sufficient oxidizing power to convert all of the NO to NO₂. Preliminary tests conducted by NIOSH (11.12., 11.15.) indicated 800 mg of oxidizer gave significantly lower recoveries for NO concentrations greater than 12 ppm. The SKC tubes tested for this evaluation (Method No. ID-190) contained approximately 1 g oxidizer per tube.

10. Discussion

The data generated during the validation indicate this method is an acceptable alternative to the polarographic method. The ion chromatographic method offers an accurate and precise determination of compliance with the OSHA 25 ppm TWA PEL for NO. A concentration-dependent conversion factor is required in calculations. Although data was not presented in this backup report regarding sorbent contamination, previous studies have indicated serious contamination problems (11.2., 11.16.). The molecular sieve solid sorbent must be washed with deionized water before impregnation and tube packing. This water washing will remove any soluble contaminants such as chloride or nitrite salts present in the molecular sieve. An attempt to identify the NO₂-TEA reaction products has been performed (11.17.); however, future work needs to be conducted to further identify and characterize the mechanism and conversion factors of this reaction.

11. References

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Table 1
Analysis - Nitric Oxide

μg^* Taken	μg^* Found	F/T	N	Mean	Std Dev	CV	AE
<u>(0.5 × PEL)</u>							
103.04	105.19	1.0209					
103.04	110.45	1.0719					
103.04	105.26	1.0215					
103.04	117.47	1.1400					
103.04	113.68	1.1033					
103.04	111.08	1.0780					
			6	1.073	0.046	0.043	15.9
<u>(1 × PEL)</u>							
206.09	226.24	1.0978					
206.09	239.92	1.1642					
206.09	226.80	1.1005					
206.09	241.83	1.1734					
206.09	215.14	1.0439					
206.09	210.37	1.0208					
			6	1.100	0.062	0.056	21.2
<u>(2 × PEL)</u>							
412.17	415.69	1.0085					
412.17	447.42	1.0855					
412.17	422.43	1.0249					
412.17	429.73	1.0426					
412.17	448.54	1.0882					
412.17	424.95	1.0310					
			6	1.047	0.033	0.031	11.0

* Results are listed as micrograms nitric oxide. These values already have the Conversion Factor applied.

F/T	=	Found/Taken = Desorption Efficiency
AE	=	Analytical Error (±%)
Bias	=	+0.073
CV ₁ (Pooled)	=	0.045
Analytical Error (Total)	=	±16.3%

Table 2
Sampling and Analysis - Nitric Oxide

ppm* Taken	ppm* Found	F/T	N	Mean	Std Dev	CV	OE
<u>(0.5 × PEL)</u>							
13.04	10.70	0.8206					
13.04	12.57	0.9640					
13.04	12.55	0.9624					
13.04	12.58	1.0560					
13.04	13.77	1.1403					
13.04	14.87	1.0867					
13.04	14.17						
			7	0.999	0.105	0.105	21.1
<u>(1 × PEL)</u>							
25.93	27.04	1.0428					
25.93	26.51	1.0224					
25.93	26.23	1.0116					
25.93	28.99	1.1180					
25.93	28.92	1.1153					
25.93	29.55	1.1396					
			6	1.075	0.056	0.052	17.8
<u>(2 × PEL)</u>							
50.52	54.02	1.0693					
50.52	48.50	0.9600					
50.52	48.77	0.9654					
50.52	48.29	0.9559					
50.52	57.02	1.1287					
50.52	55.49	1.0984					
50.52	52.87	1.0465					
			7	1.032	0.072	0.069	17.1

* Results are listed as ppm nitric oxide

F/T	=	Found/Taken
OE	=	Overall Error (±%)
Bias	=	+0.033
CV ₂ (Pooled)	=	0.080
CV _T (Pooled)	=	0.082
Overall Error (Total)	=	±19.7%

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

Sample No.	µg NO Found in		% Collection Efficiency
	First Tube	Second Tube	
1	277.95	ND	100
2	215.05	ND	100
3	254.07	ND	100
4	258.54	ND	100
5	292.02	ND	100
6	279.74	ND	100
7	265.27	ND	100

Note: (1) Sampling rate approximately 0.025 L/min at approximately 2 times the PEL for 240 min
(2) ND = None detectable <2.3 µg NO₂⁻ (10-mL sample volume)

Table 4
Breakthrough Study - Nitric Oxide (25 °C, 30% RH)

Time, Min	n	µg NO Found in		% Breakthrough
		First Tube	Second Tube	
60	3	291.18	ND	0
120	3	657.64	ND	0
180	3	960.63	ND	0
240	3	1,074.23	ND	0

Note: (1) Sampled at approximately 0.025 L/min flow rate - pump flow rates were slightly different from sample to sample (2) Generation concentration = 200 ppm NO (3) n = number of samples(4) ND = None detectable <2.3 µg NO₂⁻ (10-mL sample volume)

Table 5
Storage Stability* - Nitric Oxide

Storage Day	Found µg	Air Vol (L)	Found ppm	Taken ppm	% Recovery
<u>Day 1</u>	361.30	6.45	29.77	28.45	104.6
	358.45	6.37	29.91	28.45	105.1
	374.25	6.66	29.87	28.45	105.0
			n		3
			Mean		104.9
			Std Dev		0.26
			CV		0.0025
<u>Day 3</u>	345.52	6.58	27.91	28.66	97.4
	348.59	6.45	28.72	28.66	100.2
	345.59	6.66	27.59	28.66	96.3
			n		3
			Mean		98.0
			Std Dev		2.0
			CV		0.021
<u>Day 15</u>	370.67	6.60	29.85	28.66	104.2
	339.51	6.31	28.60	28.66	99.8
	331.44	6.66	26.45	28.66	92.3
			n		3
			Mean		98.8
			Std Dev		6.01
			CV		0.061
<u>Day 30</u>	362.52	6.59	29.24	28.51	102.6
	366.26	6.40	30.42	28.51	106.7
	353.78	6.72	27.98	28.51	98.1
			n		3
			Mean		102.4
			Std Dev		4.30
			CV		0.042

* SKC sampling devices, Lot No. 444 were used

Table 6
Humidity Test (25 °C) - Nitric Oxide

% RH	30	50	80
NO Found, ppm	22.94	27.04	26.73
	23.51	26.51	26.54
	22.60	26.23	25.49
	22.67	28.99	25.70
	26.11	28.92	31.13
	24.87	29.55	27.81
	25.18		
N	7	6	6
Mean, ppm	23.98	27.87	27.23
Std Dev, ppm	1.40	1.44	2.08
CV	0.058	0.052	0.076
Known Conc., ppm	26.17	25.93	25.78
Recovery, %	91.6	107.5	105.6

F test results:

$F_{calc} = 10.5$

$F_{crit} = 6.23$ $p < 0.01$ $df = 2, 16$

Table 7
Nitrogen Dioxide Conversion Factor

NO ₂ ppm*	n	Std Dev	CV	Average C.F.**	Source
0.82	4	0.082	0.150	0.817	1
12.89	7	0.038	0.074	0.519	1
13.72	5	0.023	0.041	0.569	1
15.74	5	0.037	0.072	0.513	2
19.85	4	0.032	0.063	0.509	2
25.20	7	0.037	0.070	0.533	1
39.65	5	0.031	0.058	0.529	2
49.79	6	0.022	0.043	0.517	1
77.85	5	0.024	0.050	0.480	2
97.90	6	0.020	0.044	0.450	1
158.57	5	0.018	0.042	0.437	2
192.57	7	0.025	0.068	0.368	1

* NO₂ ppm \Leftrightarrow NO ppmn = number of samples - collection media for all samples was 1.5% TEA solution** Average C.F. (conversion factor) was calculated from sample results assuming 100% recovery
Source 1 = NO cylinder + oxidizers
Source 2 = NO₂ permeation tubes

Table 8
Nitrogen Dioxide - Nitric Oxide Mixture Study (25 °C & 50% RH)

Air Vol, L	Nitrogen Dioxide		Nitric Oxide	
	Found ppm	Taken ppm	Found ppm	Taken ppm
7.61	5.38	5.24	25.91	28.76
8.14	5.34	5.24	26.24	28.76
9.16	5.52	5.24	28.23	28.76
7.61	5.25	5.24	25.26	28.76
8.14	6.48	5.24	34.74	28.76
9.16	4.82	5.24	23.26	28.76
n	6		6	
Mean	5.47		27.27	
Std Dev	0.55		3.99	
CV	0.101		0.146	
Recovery	104.4%		94.8%	

Table 9
Preliminary Sampling & Analysis - Nitric Oxide
Supelco Tubes

ppm* Taken	ppm* Found	F/T	N	Mean	Std Dev	CV	OE
<u>(1 × PEL Set 1)</u>							
25.96	6.07	0.234					
25.96	20.14	0.776					
25.96	22.02	0.848					
25.96	20.42	0.787					
25.96	9.99	0.385					
25.96	26.62	1.025					
25.96	10.52	0.405					
			7	0.637	0.294	0.461	128.
<u>(1 × PEL Set 2)</u>							
26.08	13.22	0.507					
26.08	22.34	0.857					
26.08	9.63	0.369					
26.08	22.47	0.862					
26.08	4.88	0.187					
26.08	8.46	0.324					
26.08	9.19	0.352					
			7	0.494	0.266	0.539	158.

* Results are listed as ppm nitric oxide

F/T = Found/Taken

OE = Overall Error (±%)

Supelco tubes, lot no. 564-07, were used.

Generation System

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

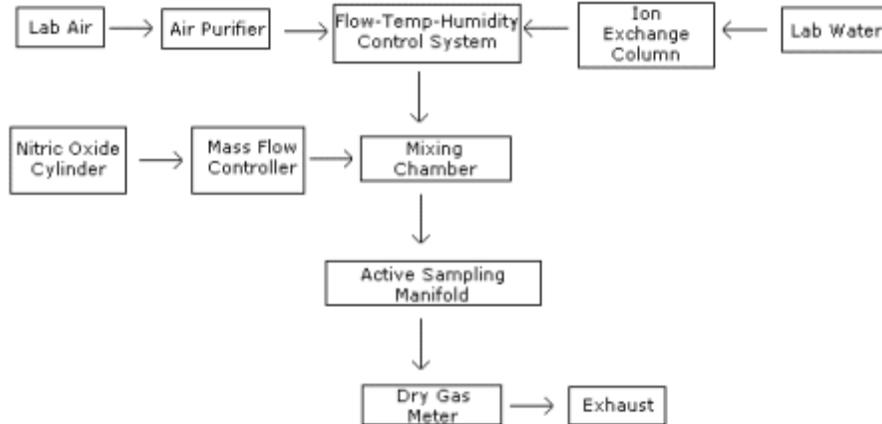


Figure 1

Proposed Conversion Factor Fits

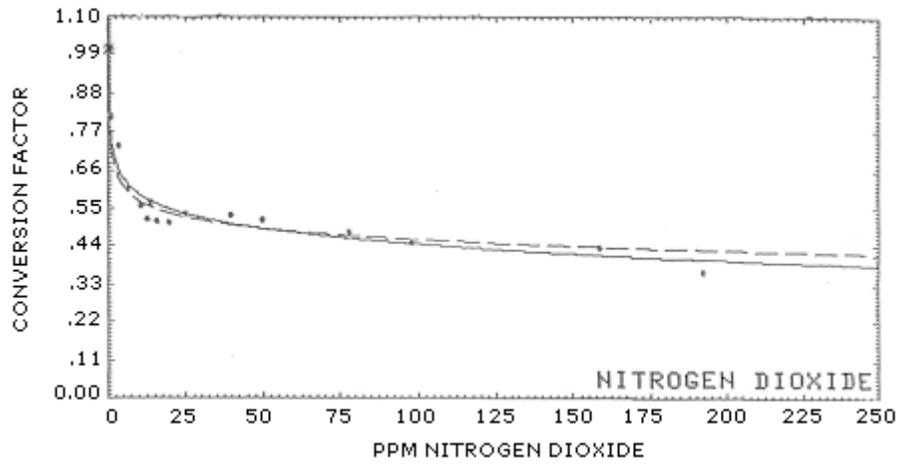


Figure 2a

Solid Line	$y = (a) + (b) \times \ln(X)$
Broken Line	$y = (a) \times (X)^p$
See Section 7 of the text for further descriptions	

Proposed Conversion Factor Fits

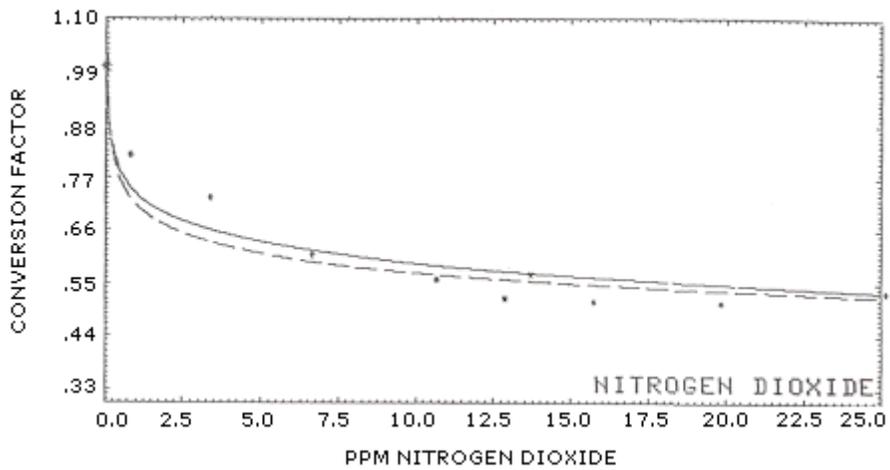


Figure 2b

Solid Line	$y = (a) + (b) \times \ln(X)$
Broken Line	$y = (a) \times (X)^p$
See Section 7 of the text for further descriptions	