

OZONE IN WORKPLACE ATMOSPHERES  
(IMPREGNATED GLASS FIBER FILTER)



---

Method Number:	ID-214															
Matrix:	Air															
OSHA Permissible Limits Final Rule Limits Time Weighted Average (TWA):	0.1 ppm*															
Short-Term Exposure Limit (STEL):	0.3 ppm*															
Transitional Limit (TWA):	0.1 ppm															
Collection Device:	An air sample is collected using a calibrated sampling pump and a two-piece polystyrene cassette containing two nitrite-impregnated glass fiber filters (IGFFs). During collection, ozone reacts with the nitrite impregnated on the filter collection device and converts it to nitrate via oxidation.															
Recommended Sampling Rate (See Special Precautions below)																
TWA:	0.25 to 0.5 liter per minute (L/min)															
STEL:	1.5 L/min															
Recommended Air Volume																
TWA:	90 L (180 min at 0.5 L/min). Longer sampling times can be used (up to 480 min) when using 0.25 L/min flow rate.															
STEL:	22.5 L (1.5 L/min for 15 min)															
Analytical Procedure:	The reaction product is extracted from the filters and blanks using deionized water and the extracts are analyzed by ion chromatography as nitrate using UV-VIS detector at 200 nm wavelength. A conductivity detector can also be used.															
Detection Limit																
Qualitative:	0.008 ppm (90-L air sample) 0.032 ppm (22.5-L air sample)															
Quantitative:	0.03 ppm (90-L air sample) 0.11 ppm (22.5-L air sample)															
Accuracy	<table><thead><tr><th></th><th><u>TWA</u></th><th><u>STEL</u></th></tr></thead><tbody><tr><td>Validated Range:</td><td>0.070 to 0.224 ppm</td><td>0.330 ppm</td></tr><tr><td>CV<sub>T</sub>(pooled):</td><td>0.045</td><td>0.054 (CV<sub>2</sub>)</td></tr><tr><td>Bias:</td><td>+0.014</td><td>-0.015</td></tr><tr><td>Overall Error:</td><td>±10.4%</td><td>±12.3%</td></tr></tbody></table>		<u>TWA</u>	<u>STEL</u>	Validated Range:	0.070 to 0.224 ppm	0.330 ppm	CV <sub>T</sub> (pooled):	0.045	0.054 (CV <sub>2</sub> )	Bias:	+0.014	-0.015	Overall Error:	±10.4%	±12.3%
	<u>TWA</u>	<u>STEL</u>														
Validated Range:	0.070 to 0.224 ppm	0.330 ppm														
CV <sub>T</sub> (pooled):	0.045	0.054 (CV <sub>2</sub> )														
Bias:	+0.014	-0.015														
Overall Error:	±10.4%	±12.3%														
Method Classification:	Validated Method															
Special Precautions:	Slight breakthrough (~7.5%) of ozone was noted at approximately 0.4 ppm. If the expected ozone (O <sub>3</sub> ) concentration is more than 0.2 ppm, the recommended sampling rate can be reduced to 0.25 L/min.															

Date: March 1995

Chemist: James C. Ku

---

\* The U.S. Court of Appeals, Eleventh Circuit, has ruled that Final Rule Limits of 29 CFR 1910.1000 be vacated. The Final Rule definition of "TWA" and "STEL" have been retained. Although the Final Rule Limits have been vacated, OSHA encourages industry and government to abide by these limits established by scientific evidence (memorandum for Directorate Heads, Office Directors and Regional Administrator from Roger Clark, Director of Compliance Programs OSHA, 3/30/93).

---

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.

---

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

## 1. Introduction

This method describes the sample collection and analysis of airborne ozone (O<sub>3</sub>). Air samples are taken in the breathing zone of workplace personnel, and analysis is performed by ion chromatography (IC) equipped with a UV-VIS and conductivity detector. Nitrate analysis by conductivity is well established since the 1970s. Both UV-VIS and conductivity detectors are suggested in this method to allow versatility and offer the possibility of excluding interferences by switching detectors. This method is not applicable for collection and analysis of bulk or wipe samples.

### 1.1 History

Many previous attempts were made to measure ozone in occupational environments. All have various shortcomings and demonstrate the past degree of difficulty in developing an adequate method. A chronological presentation of some of the methods OSHA has used or evaluated is discussed below:

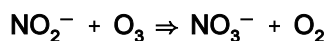
- 1.1.1 Detector tubes: The major drawback of detector tubes is the need to use a cumbersome statistical technique to assess Time Weighted Average (TWA) exposures.
- 1.1.2 KI and AKI methods: An early method to determine occupational exposure to ozone in the workplace involved collection in neutral potassium iodide (KI) solution and analysis by colorimetry (Ref. 5.1). A modification involved collecting samples in an alkaline potassium iodide (AKI) solution and analyzing them by colorimetry after acidifying with sulfamic acid (Ref. 5.2). It has been reported (Ref. 5.3) that the reaction of ozone with AKI to produce iodine is not quantitative and is concentration dependent. Therefore, a conversion equation must be used to convert the values equivalent to the neutral KI method.
- 1.1.3 OSHA KIBRT (potassium iodide-potassium bromide-sodium thiosulfate) (Ref. 5.4): This method resolved some of the stability and interference problems associated with prior methods which used KI.
- 1.1.4 Trans-stilbene (Ref. 5.5): Previous work has been reported using glass beads coated with trans-stilbene for collecting ozone (Ref. 5.6). Preliminary tests showed that this method was affected by humidity as low as 50% relative humidity (RH) (Ref. 5.7). To compensate for this humidity problem, an impinger sampling method using a collection solution (as stated in chronological list below) was developed at the OSHA-SLTC (Ref. 5.5). Although this method could be used under controlled conditions as a reference method in the laboratory, the 90% acetonitrile in water is flammable and should not be used for field use. Alternative non-flammable collection solutions were not found during this study.
- 1.1.5 Direct-Readers AID Model 560 (Ref. 5.8) or AED-030 (Ref. 5.9): A strip chart recorder to record data was used to document for both direct-readers compliance monitoring. The AID Model 560 also required a battery recharge every 8 to 10 hours, making it inconvenient. The AED-030 can be used for only 4 to 5 hours with batteries; a line voltage power converter or replacement batteries is necessary for longer periods.
- 1.1.6 Recently, it has been reported (Ref. 5.10) that the measurement of ozone can be done using a commercially available passive sampling device containing a nitrite-impregnated filter. According to the manufacturer, the shelf-life of the sampling portion of the passive device is conservatively 4 weeks from the nitrite impregnation date to the analysis date. Based on the nitrite principle, OSHA Method ID-214 was developed as an active sampling system. The commercially available passive system was initially tested and some of the data is included in the backup report (Section 4.) Because of sensitivity (Section 4.10) and potential interference considerations of the passive sampler, this active sampling method is more suitable for OSHA compliance purposes.

A chronological summary of OSHA SLTC ozone monitoring techniques is shown below:

Date	Method	Principle	Collection Medium	Major Advantages	Major Disadvantages
1960s - present	Detector tubes	Oxidation of indigo by ozone resulting in white color	Direct-read	Simple, rapid	Interferences, more a spot check for exposure measurement
Before 1977	1% Neutral buffered KI	Reaction with KI	1% KI, phosphate buffer, pH=6.8	Simple, rapid, and sensitive	Bubbler, unstable, and interferences from all oxidants
1977 - 80	Alkaline KI	Reaction with KI	1% KI, 1.0 N NaOH, pH>11	Simple, rapid, and sensitive	Bubbler, unstable, sampling rate dependence, and interferences from all oxidants
1983 - 92	Ozone meter (AID Model 560)	Chemiluminescence	Direct reading instrument	Very sensitive, direct-reading, very specific	No data logging and bulky instrument requiring ethylene (flammable gas) or Ethychem (ethylene in CO <sub>2</sub> )
1986	Neutral buffered (KIBRT)	Reaction with KI and Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> . Measurement of excess I <sub>2</sub>	1% KI, a known amount of thiosulfate, 2% KBr	Simple, rapid sensitive, stable and some independence from sampling rate	Bubbler, interferences from all oxidants. Potential contamination.
1990 - 91 (Lab use only)	Glass beads trans-stilbene	Reaction with olefins	Glass beads coated with trans-stilbene	Simple, rapid, sensitive and O <sub>3</sub> specific	Recovery dependent on humidity
1990 - 91 (Lab use only)	trans-stilbene and mesitol	Reaction with olefins	0.05% trans-stilbene + 0.5% mesitol in a mixture of acetonitrile/water (9:1)	Simple, rapid, sensitive and O <sub>3</sub> specific	Flammable liquid, bubbler used for sample collection
1992 - present	Ozone meter (AED-030)	Semi-conductor sensor	Direct reading instrument	Simple, rapid, sensitive and easy to use	No data logging capacity, instrument tends to drift
This method	IGFF	Reaction with nitrite	Nitrite-coated IGFFs	Simple, rapid, sensitive	Interference from SO <sub>2</sub>

## 1.2 Principle

Ozone is collected using two nitrite-impregnated glass fiber filters (IGFFs). The second IGFF serves as a backup filter. The collected O<sub>3</sub> converts nitrite (NO<sub>2</sub><sup>-</sup>) to nitrate (NO<sub>3</sub><sup>-</sup>) via oxidation as shown by the following chemical reaction:



The resultant NO<sub>3</sub><sup>-</sup> is analyzed by IC using a UV-VIS detector at a wavelength of 200 nm. A gravimetric conversion factor is used to calculate the amount of O<sub>3</sub> collected from the amount of NO<sub>3</sub><sup>-</sup> found.

## 1.3 Advantages and Disadvantages

1.3.1 This method has adequate sensitivity for determining compliance with the OSHA Permissible Exposure Limit (PEL) of 0.1 ppm for O<sub>3</sub> exposure. The method is also capable of monitoring Food and Drug Administration limit of 0.05 ppm O<sub>3</sub> in enclosed spaces (21 CFR 801.415). The U.S. Environmental Protection Agency (EPA) has established a National Ambient Air Quality Standard (NAAQS) for O<sub>3</sub> at 0.12 ppm for a 1-hour average. The method is capable of monitoring for the EPA limit provided a sampling rate of at least

0.5 L/min is used. All three limits have been used to determine Indoor Air Quality (IAQ) in relation to O<sub>3</sub> exposure.

- 1.3.2 The method is simple, rapid, and easily automated.
- 1.3.3 The method is “relatively” specific for O<sub>3</sub> (as NO<sub>3</sub><sup>-</sup>) in the presence of other nitrogen-containing substances, such as nitrogen dioxide (NO<sub>2</sub>).
- 1.3.4 The sampling device is small, portable, and contains no liquid.
- 1.3.5 Desorption and preparation of samples for analyses involve simple procedures and equipment.
- 1.3.6 Samples can be analyzed using either a UV-VIS or conductivity detector. The majority of the validation was performed using a UV-VIS detector.
- 1.3.7 One disadvantage is that sulfur dioxide (SO<sub>2</sub>) gas and soluble particulate nitrate compounds interfere when collected on the same IGFFs (Section 4.9). A pretube containing a chromate compound can be used to remove any SO<sub>2</sub> and allow O<sub>3</sub> to react with the IGFFs. Significant levels of soluble nitrate substances should not normally be encountered in an occupational setting unless these substances are in use. Examples of soluble substances are potassium or sodium nitrate.
- 1.3.8 Another disadvantage of the method is the tedious preparation and storage of the IGFFs (Section 2.1.3).

#### 1.4 Methods Performance

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

- 1.4.1 This method was validated over the concentration range of 0.070 to 0.224 ppm. An air volume of 90 L and a flow rate of 0.5 L/min were used.
- 1.4.2 The qualitative detection limit was 0.37 µg/mL or 1.85 µg (as NO<sub>3</sub><sup>-</sup>) when using a 5-mL solution volume. This corresponds to 0.008 ppm O<sub>3</sub> for a 90-L air volume.
- 1.4.3 The quantitative detection limit was 1.25 µg/mL or 6.25 µg (as NO<sub>3</sub><sup>-</sup>) when using a 5-mL solution volume. This corresponds to 0.03 ppm O<sub>3</sub> for a 90-L air volume. A 50-µL sample loop and a detector setting of 2 absorbance units (AU) for full-scale output were used.
- 1.4.4 The sensitivity of the analytical method, when using the instrument parameters listed in Section 3.6.3, was calculated from the slope of a linear working range curve (0.5 to 10.0 µg/mL NO<sub>3</sub><sup>-</sup>). The sensitivity was 3.7 × 10<sup>5</sup> area units per 1 µg/mL. A Dionex Series 4500i ion chromatograph with a Linear UVIS-206 UV detector and AI450 computer software was used (Dionex, Sunnyvale, CA).
- 1.4.5 The total pooled coefficient of variation (CV), bias, and total overall error (OE) for TWA and STEL-type determinations are shown below:
 

	TWA	STEL
CV	0.045	0.054
Bias	+0.014	-0.015
OE	±10.4%	±12.3%
- 1.4.6 The collection efficiency at 2 times the PEL was 100%. Samples were collected from a generated test atmosphere of 0.20 ppm O<sub>3</sub> for 180 min at 0.5 L/min.
- 1.4.7 For TWA measurements, two breakthrough tests were performed at concentrations of 0.22 and 0.4 ppm O<sub>3</sub>. Using a sampling time of 240 min and an average sample flow rate of 0.5 L/min, no breakthrough was found at a concentration of 0.22 ppm O<sub>3</sub>, and the average

breakthrough was 7.5% at a concentration of 0.4 ppm O<sub>3</sub>. However, no breakthrough was found at a concentration of 0.6 ppm O<sub>3</sub> after reducing the flow rate to approximately 0.25 L/min and a sampling time of 240 min. For STEL, no breakthrough was found at a concentration of 0.33 ppm O<sub>3</sub> using a sampling time of 15 min and an average sample flow rate of 1.5 L/min.

- 1.4.8 Samples can be stored at ambient (20 to 25 °C) temperature for a period of 30 days. Results show the mean sample recovery after 30 days storage was within ±10% of results at Day 0.
- 1.4.9 The mean blank recovery after 30 days storage was 5 µg compared to 1.5 µg on Day 0 (as total nitrate). A final solution volume of 5 mL was used.

## 1.5 Interferences

- 1.5.1 Sampling: Because O<sub>3</sub> is analyzed as nitrate, particulate nitrate compounds may interfere (positive) in the analysis if collected on the same IGFFs. Sulfur dioxide in the presence of O<sub>3</sub> will also interfere (negative). If interference from SO<sub>2</sub> is expected, an oxidizer pretube, such as the tube commonly used for converting NO to NO<sub>2</sub> (OSHA Method ID-182 or ID-190), can be used to effectively remove SO<sub>2</sub> and allow O<sub>3</sub> to pass through the IGFFs. These oxidizer tubes must be passivated in the ozone atmosphere prior to use.
- 1.5.2 Analytical: Any substance that absorbs UV at 20 nm and has the same retention time as NO<sub>3</sub><sup>-</sup> is an interference when using the UV-VIS detector. If the possibility of an interference exists, changing the analytical conditions (detector settings, chromatographic column, eluent flow rate, strength, etc.) may circumvent the problem. Substances that have the same retention time as NO<sub>3</sub><sup>-</sup> and are conductive may interfere when analyzed by conductivity. Most interferences may be resolved by changing detectors (i.e., changing from conductivity to UV-VIS or vice-versa).

## 1.6 Industrial Uses and Products of Ozone (Ref. 5.11)

- 1.6.1 Ozone is used mainly for: purification of drinking water; industrial waste treatment; deodorization of air and sewage gases; bleaching of waxes, oils, wet paper, and textile; production of peroxides; and as a bactericide.
- 1.6.2 Ozone is also used as: an oxidizing agent in several chemical processes (acids, aldehydes, and ketones from unsaturated fatty acids); steroid hormone formation; removal of chlorine from nitric acid; and oxidation of phenols and cyanides.

## 1.7 Physical and Chemical Properties (Refs. 5.11-5.12)

Ozone has a pungent odor, is a strong irritant, and is highly toxic by inhalation. It is strong oxidizing agent and a dangerous fire and explosion risk when in contact with organic materials. It is more soluble in water than oxygen; however, the minimal solubility results in the liberation of significant amounts of ozone after water is purified with ozone.

CAS No.	10028-15-6
Chemical formula	O <sub>3</sub>
Formula weight	47.997
Specific gravity	1.6 (liquid) @ -183 °C
Melting point	-192 °C
Boiling point	-112 °C
Vapor density (air = 1)	1.65
Synonym	Triatomic oxygen
Appearance and odor	Colorless at concentrations noted in industry. Pungent characteristic odor usually associated with electric sparks.

## 1.8 Toxicology (Ref. 5.13)

---

Information listed within this section is a synopsis of current knowledge of the physiological effects of O<sub>3</sub> and is not intended to be used as a basis for OSHA policy.

---

Ozone is highly injurious and potentially lethal to experimental animals at concentrations as low as a few parts per million (ppm). A study in which young mice were exposed to 1 ppm ozone for 1 or 2 days reported damage to alveolar tissue. Human populations chronically exposed to lower concentrations of ozone were observed to have adverse changes in lung function. Human volunteers exposed to 0.5 ppm ozone for 3 hours per day, 6 days per week, for 12 weeks showed significant adverse changes in lung function. Another report showed a 20 percent reduction in timed vital lung capacity in persons exposed to average concentrations of ozone of 1.5 ppm for 2 hours. Welders exposed to maximal ozone concentrations of 9 ppm were observed to have pulmonary congestion. Recent studies indicate ozone may contribute to inflammation in human bronchial tubes. Further information regarding toxic effects of ozone can be found in Ref. 5.12.

## 2. Sampling

---

Note: Particulate nitrate compounds or SO<sub>2</sub>, gas interfere in the analysis of NO<sub>3</sub><sup>-</sup> if collected on the same IGFFs. However, if interference from SO<sub>2</sub> is expected, a pretube, such as the tube used for converting NO to NO<sub>2</sub>, can be used to effectively remove SO<sub>2</sub>, and allow O<sub>3</sub> to pass through to the IGFFs. If the amount of SO<sub>2</sub> in the area to be sampled is unknown, detector tubes (OSHA SLTC Product Evaluation No. 12 for recommended tubes) can be used to screen the area or a long-term sampling method (OSHA SLTC Method ID-200) can be used to determine if SO<sub>2</sub> is present prior to O<sub>3</sub> sampling. If particulate nitrate compounds are present in the air, contact OSHA-SLTC. If these compounds are soluble and present in sufficient quantity, an alternate method employing direct-reading instruments may have to be used.

---

### 2.1 Equipment

- 2.1.1 Calibrated personal sampling pumps capable of sampling within ±5% of the recommended flow rate of 0.5 L/min are used.
- 2.1.2 Tygon or other flexible tubing for connecting pumps to samples.

### 2.1.3 Sampling media:

Impregnated glass fiber filters (IGFFs) are used for sample collection and are obtained from OSHA-SLTC for OSHA use. The filters can also be prepared as explained below:

---

Note: Before impregnation, glass fiber filters (GFFs) must be thoroughly cleaned with deionized water (DI H<sub>2</sub>O) to remove any trace amounts of soluble nitrate compounds. Filter impregnation requires the use of very pure chemicals, and careful handling of both the chemicals and IGFFs is required to avoid contamination from soluble nitrate-containing substances. After preparation, the IGFFs must be stored in clean cassettes and sealed with scaling bands before use. A conservative shelf-life of 4 weeks should be observed.

---

- a) Glass fiber filters (GFFs), 37-mm (Prod. no. 61652, Type A/E, 500/pkg, Gelman Sciences, Ann Arbor, MI)
- b) Glass beakers, 400 - 500-mL and 10 - 15-mL (or 25-mL Erlenmeyer flasks)
- c) Oven, 0 - 200 °C
- d) Forceps
- e) Cassette gel sealing bands
- f) Plastic end plugs
- g) Two-section polystyrene cassettes, 37-mm diameter (part no. MAWP037 AO, Millipore Corp., Bedford, MA)
- h) Principal chemicals - These should be at least reagent grade or better to avoid nitrate contamination:
  - Sodium nitrite (NaNO<sub>2</sub>), 97+%
  - Potassium carbonate (KCO<sub>3</sub>), 99%
  - Glycerol, 99.5%

---

Impregnated glass fiber filters (IGFFs) are prepared by chemically treating 37-mm GFFs according to the following procedure:

---

- a) Prepare an "impregnating solution" by adding 0.3 g NaNO<sub>2</sub>, 0.28 g K<sub>2</sub>CO<sub>3</sub>, and 1 mL of glycerol to 100 mL DI H<sub>2</sub>O.
- b) Clean approximately 100 GFFs thoroughly by carefully placing the filters using forceps into a thoroughly cleaned beaker (1- or 2-L) with approximately 400-500 mL DI H<sub>2</sub>O. Decant and rinse by adding another 400 to 500 mL DI H<sub>2</sub>O. Decant, and then dry the filters in the oven at 100 °C for 60 min or until completely dry.
- c) Set each GFF on the top of a 10-mL beaker or a 25-mL Erlenmeyer flask.
- d) Slowly spike 0.4 mL of impregnating solution on each GFF making sure the entire filter is saturated.
- e) Carefully place each beaker or Erlenmeyer flask (on which each IGFF is sitting) into an oven and dry at 100 °C for 30 min.
- f) Carefully and slowly remove all beakers or Erlenmeyer flasks from the oven and allow to cool to room temperature. (Note: Do not allow the filters to stand once they have cooled to room temperature and prior to placement in cassettes. They will react with any atmospheric ozone present.) Using forceps, immediately place two IGFFs into a clean cassette, seal with plastic end plugs, place a shrinkable gel band around each cassette, and record the date. (Note: The sides of the IGFF have different textures. One side is rough, the other is woven and has a waffle-like appearance. Make sure the rough sides of two IGFFs are face up, i.e., facing the incoming sample.)
- g) IGFFs prepared in this fashion are stable for at least 28 days (Section 4.10).

2.1.4 A stopwatch and bubble tube or meter to calibrate pumps.

2.1.5 Various lengths of polyvinyl chloride (PVC) tubing to connect sampling tubes to pumps.

2.1.6 Oxidizer tube for removing SO<sub>2</sub> in the sampled air

---

If there is reason to suspect the sampled air could contain SO<sub>2</sub>, an oxidizer tube must be used to remove the SO<sub>2</sub>. See Figure 1 below and also Section 4.9 for further details.

---

Oxidizer tubes normally used to convert nitric oxide to nitrogen dioxide will suffice; however, the contents of the tubes must be passivated with O<sub>3</sub> prior to use. Oxidizer tubes can be obtained from SKC Inc., Eighty Four, PA as a Special Order item. The manufacturer or the user can passivate the oxidizer tubes prior to use, and a shelf-life after passivation of one to two years should be observed. Passivation requires special ozone-generating equipment. Oxidizer tubes and any Tygon tubing used in sampling must be conditioned with ozone using the following procedure (Note: The O<sub>3</sub> generation system used to validate this method and condition the oxidizer tubes and Tygon tubing is further discussed in Section 4.2.1. Other comparable systems can be used.):

- 1) Connect one end of each open oxidizer tube to the ozone generation system with short pieces of Tygon tubing. (Note that this tubing will also be passivated and should be used as the oxidizer-cassette connector when taking a sample using an oxidizer tube.)
- 2) Set the O<sub>3</sub> concentration for the generation system at approximately 0.1 ppm.
- 3) Set the sampling pumps at approximately 0.5 L/min flow rates. Connect the other end of the open oxidizer tube to each sampling pump using Tygon tubing.
- 4) Condition the oxidizer tubes for 4 h. Stop the sampling pumps and cap the tubes using plastic caps or flame seal. The shelf-life of the oxidizer should be 1 to 2 years.

## 2.2 Sampling Procedure

- 2.2.1 Remove both plastic end plugs from the cassette and connect the cassette to the calibrated sampling pump, making sure the sampled air enters the rough side of the IGFF. Use an oxidizer tube only if SO<sub>2</sub> is suspected of being present in the sampled air (Figure 1). Place the sampling device on the employee such that air is sampled from the breathing zone.

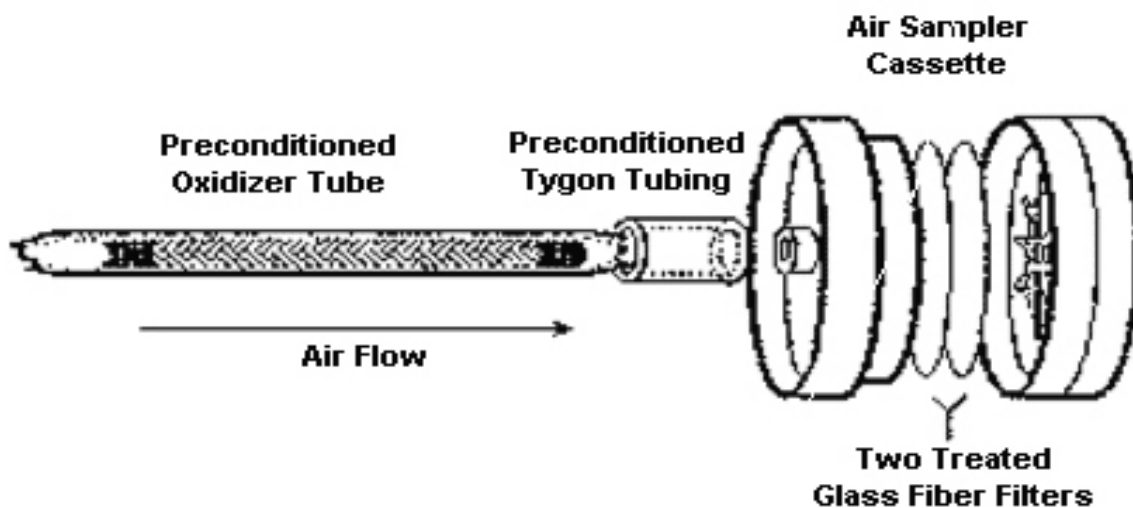


Figure 1. Ozone sampler with oxidizer tube.

- 2.2.2 Use a flow rate of 0.5 L/min and a sampling time of 180 min. Take additional samples as necessary. A 0.25 L/min flow rate and a sampling time up to 480 min can also be used.
- 2.2.3 After sampling, immediately replace both plastic end plugs tightly in the cassette and apply OSHA Form 21 seals in such a way as to secure the end plugs.



- 2.2.4 Record the sampling conditions such as sampling time, air volume, flow rate, etc. on the OSHA 91A. When other compounds are known or suspected to be present in the air, record such information and transmit with the samples.
- 2.2.5 Handle a blank filter and cassette in exactly the same manner as the sample cassettes except that no air is drawn through it. Use the same lot and preparation date of IGFF/cassettes for blank and collected samples. Prepare at least one blank filter and cassette for each batch of ten samples.
- 2.2.6 Send the samples and blanks to the laboratory as soon as possible with the OSHA 91A paperwork requesting ozone analysis.

### 3. Analysis

#### 3.1 Safety Precautions

- 3.1.1 Review appropriate IC instrument manuals, UV-VIS detector or spectral array detector maintenance manual, and the Standard Operating Procedure (SOP) for proper instrument operation (Ref. 5.14).

---

Note: The SOP is a written procedure for a specific instrument. It is suggested that SOPs be prepared for each type of instrument used in a lab to enhance safe and effective operation.

---

- 3.1.2 Observe laboratory safety regulations and practices.
- 3.1.3. Review any MSDSs provided with reagents and samples. Observe all precautions. Many chemicals are hazardous. Use appropriate personal protective equipment such as safety glasses, goggles, face shields, gloves, and lab coat when handling these chemicals.

#### 3.2 Equipment

- 3.2.1 Ion chromatograph (Model 4000i or 4500i Dionex, Sunnyvale, CA) equipped with a UV-VIS detector (Linear UVIS-206, Multiple wavelength detector, Linear Instruments Corporation, Reno, NV) or a conductivity detector.
- 3.2.2 Automatic sampler (Dionex Model AS-1) and 0.5-mL sample vials/caps (Dionex part no. 38011).
- 3.2.3 Laboratory automation system: Ion chromatograph interfaced with a data reduction system (AI450, Dionex).
- 3.2.4 Separator and guard columns, anion (Model HPIC-AS9 and AG9, Dionex).
- 3.2.5 Forceps.
- 3.2.6 Disposable beakers (10 and 50 mL).
- 3.2.7 Cassette opener (SKC E-Z Opener, Cat. No. 225-13-5, SKC) or similar tool such as a coin or a screwdriver.
- 3.2.8 Disposable syringes (1 mL).
- 3.2.9 Syringe prefilters, 0.5- $\mu$ m pore size (part no. SLSR 025 NS, Millipore Corp., Bedford, MA).

---

Note: Some syringe prefilters are not cation- or anion-free. Blank reagent solutions should be filtered and analyzed first to determine potential contamination and suitability with the analyte.

---

- 3.2.10 Miscellaneous volumetric glassware: Pipettes, volumetric flasks, Erlenmeyer flasks, graduated cylinders, and beakers.
- 3.2.11 Equipment for eluent degassing (vacuum pump, ultrasonic bath).
- 3.2.12 Analytical balance (0.01 mg).
- 3.2.13 Scintillation vials, 20 mL, with polypropylene- or Teflon-lined caps.
- 3.2.14 Treated glass fiber filters (IGFFs from Section 2.1.3) for spiking or matrix matching (if necessary).
- 3.3 Reagents - All chemicals should be at least reagent grade.
- 3.3.1 Principal reagents:
- Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), 99%  
 Sodium bicarbonate ( $\text{NaHCO}_3$ ), 99%  
 Sodium nitrate ( $\text{NaNO}_3$ ), 99.9%  
 Deionized water (DI  $\text{H}_2\text{O}$ )
- 3.3.2 Eluent (1.0 mM  $\text{Na}_2\text{CO}_3$  + 1.0 mM  $\text{NaHCO}_3$ ):
- Dissolve 0.424 g  $\text{Na}_2\text{CO}_3$  and 0.336 g  $\text{NaHCO}_3$  in 4.0 L DI  $\text{H}_2\text{O}$ . Sonicate this solution and degas under vacuum for 15 min.
- 3.3.3 Nitrate ( $\text{NO}_3^-$ ) stock standard (1,000  $\mu\text{g}/\text{mL}$ ):
- Dissolve and dilute 1.3710 g of  $\text{NaNO}_3$  to 1.0 L with DI  $\text{H}_2\text{O}$ . Prepare every 6 months.

---

Note: The laboratory should have an effective, independent quality control (QC) program in place and QC samples of the analyte should be routinely analyzed along with field samples. Depending on the capabilities of the program, QC samples can either be generated using the collection media and substance ( $\text{O}_3$ ) under controlled conditions, or media can be spiked with the analyte ( $\text{NO}_3^-$ ). If QC samples are not routinely prepared and analyzed, two different standard stock solutions should always be prepared and these solutions should routinely be compared to each other. Always prepare the stocks from two different sources or, as last resort, from different lots.

---

- 3.3.4 Nitrate ( $\text{NO}_3^-$ ) standard solutions, 100, 10, and 1  $\mu\text{g}/\text{mL}$ : Pipette appropriate volumes of the 1,000  $\mu\text{g}/\text{mL}$  as  $\text{NO}_3^-$  stock standard into volumetric flasks and dilute to the mark with eluent. Prepare monthly.
- 3.4 Working Standard Preparation - Prepare fresh prior to beginning the analysis.
- 3.4.1 Prepare  $\text{NO}_3^-$  working standards in eluent. A suggested scheme for preparing a series of working standards using 10-mL final solution volumes is shown below:

working std ( $\mu\text{g}/\text{mL}$ )	std solution ( $\mu\text{g}/\text{mL}$ )	aliquot (mL)	eluent added (mL)
0.5	1.0	5.0	5.0
1.0*	1.0	-	-
2.0	10.0	2.0	8.0
5.0	10.0	5.0	5.0
10.0	10.0	-	-

\* Already prepared in Section 3.3.4

- 3.4.2 To prepare each working standard (Working Std) listed above, transfer an appropriate amount of the Std Solution to a disposable beaker, pipette an appropriate aliquot (Aliquot)

of the specified standard solution (prepared in Section 3.3.4) from the disposable beaker to an appropriate container (scintillation vial, Erlenmeyer flask, etc.). Add the specified amount of eluent (Eluent Added).

- 3.4.3 As an alternative, pipette each aliquot into a 10-mL volumetric flask and dilute to volume with eluent.

### 3.5 Sample Preparation

- 3.5.1 Carefully open each cassette with a cassette opener (or similar tool, such as a coin or a screwdriver), remove each IGFF and transfer each filter using a clean forceps into separate 20-mL scintillation vials.

- 3.5.2 Pipette 5.0 mL of DI H<sub>2</sub>O into each vial. Make sure the filter is wetted. Cap the vials using polyethylene-lined plastic caps.

---

Note: Alternate desorption volumes can be used and are dependent on the analytical sensitivity desired. For most industrial hygiene samples, 5-mL volumes will allow for analysis of ozone (as NO<sub>3</sub><sup>-</sup>) within the range of the standards specified.

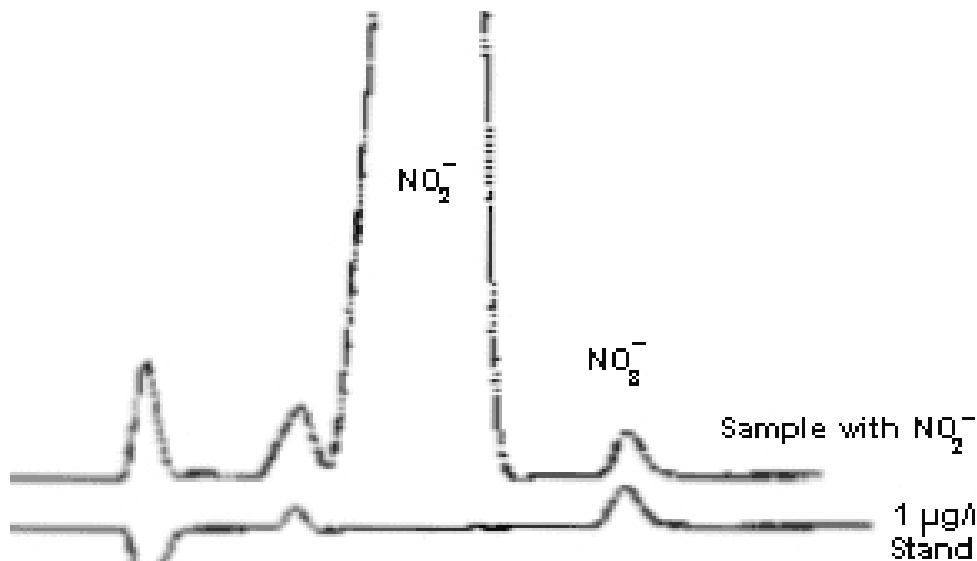
---

- 3.5.3 Allow the samples to sit for at least 15 min. Occasionally swirl each solution.

- 3.5.4 If the sample solutions contain particulate, remove the particles using a prefilter and syringe.

### 3.6 Analysis

It is imperative that the large nitrite peak (from the sampling media) is adequately separated from the nitrate peak. This can be assured by desorbing an IGFF (Section 3.2.14) with eluent, spiking the solution with a known amount of nitrate working standard, and analyzing this solution prior to analysis. The chromatogram shown below (Comparison of a Standard and a Sample) demonstrates the peaks obtainable from a sample and a standard without any matrix-matching. Peak characteristics of the nitrate in the standard and sample are similar, retention times appear very close, and there is adequate separation of nitrite and nitrate. If a comparison of a spiked sample and a nitrate standard indicates poor separation or significantly different NO<sub>3</sub><sup>-</sup> retention times, matrix-matching or a change in analytical conditions should occur. A new column could be used or the eluent strength may be changed to facilitate separation. If matrix-matching of standards and samples is the only alternative, standards should be prepared with treated filters in the same fashion as samples.



- 3.6.1 Pipette or pour a 0.5- to 0.6-mL portion of each standard or sample into separate automatic sampler vials. Place a filtercap into each vial. The large filter portion of the cap should face the solution.
- 3.6.2 Load the automatic sampler with labeled samples, standards, and blanks.
- 3.6.3 Set up the ion chromatograph in accordance with the SOP (Ref. 5.14). Typical operating conditions for a Dionex 4000i or 4500i with a UV-VIS detector (Spectral Array detector) and an automated sampler are listed below:

Ion chromatograph with UV detector\* at 200 nm wavelength

Eluent:	1.0 mM NaCO <sub>3</sub> /1.0 mM NaHCO <sub>3</sub>
Column temperature:	ambient
Anion precolumn:	AG9
Anion separator column:	AS9
Output range:	2 absorbance units full scale (AUFS)
Rise time:	5 sec
Sample injection loop:	50 µL

Pump

Pump pressure:	~900 psi
Flow rate:	2 mL/min

Chromatogram

Run time:	5 min
Peak retention time:	~3.00 min for NO <sub>3</sub> <sup>-</sup>

\*For detection using a conductivity detector, output range and rise time are not used. A sensitivity setting on the conductivity detector of 0.1 µS is used. All other settings are similar.

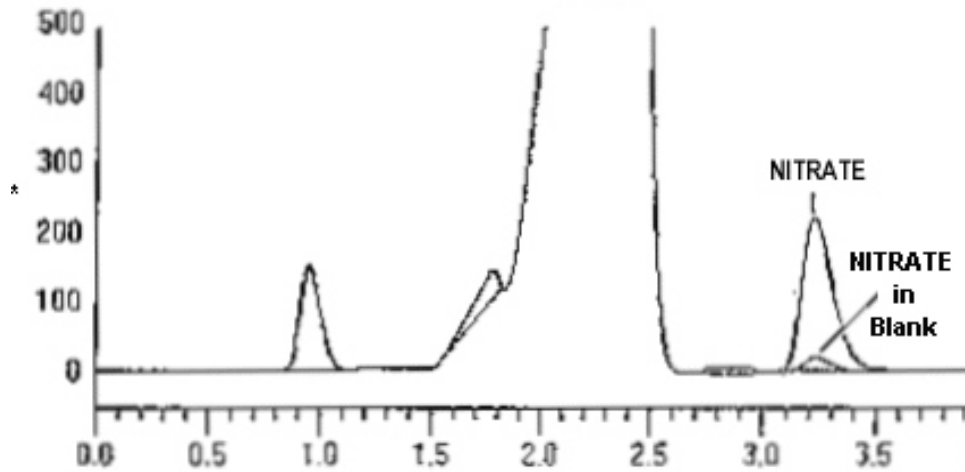
Soluble nitrate compounds can interfere when using either UV or conductivity detector. Response to nitrate using either detector is similar and appears to be dependent on column conditions, eluent strength, and sensitivity settings.

3.6.4 Analyze samples, standards, and blanks according to SOP (Ref. 5.14).

### 3.7 Calculations

3.7.1 After the analysis is completed, retrieve the peak areas or heights. Obtain hard copies of chromatograms from a printer. A chromatogram of a sample collected at an ozone concentration of approximately 2 times the PEL for 180 min is shown below:

ret time	component name	concentration	height	area
3.22	nitrate	6.142 µg/mL	218782	2202892



\*Relative absorbance units using a UV-VIS detector

Note: The nitrate normally contained in a blank is only shown for illustration purposes. Peak heights, peak area, and retention times are instrument dependent and were obtained using equipment specified in Section 3.2.

3.7.2 Prepare a concentration-response curve by plotting the peak areas or peak heights versus the concentration of the  $\text{NO}_3^-$  standards in µg/mL.

3.7.3 Determine total µg for each sample and blank. Perform a blank correction for each IGFF. Subtract the total µg blank value from each total µg sample value.

$$A_b = (\mu\text{g/mL NO}_3^-)_b \times (\text{Sol Vol})_b \times (\text{CF})$$

$$A_s = (\mu\text{g/mL NO}_3^-)_s \times (\text{Sol Vol})_s \times (\text{CF})$$

$$A = A_s - A_b$$

Then calculate the air concentration of  $\text{O}_3$  (in ppm) for each air sample:

$$\text{ppm O}_3 = \frac{A \times (\text{Mol Vol})}{AV \times (\text{Mol Wt})}$$

where:

$A_b$  = Total µg  $\text{O}_3$  in blank

$A_s$  = Total µg  $\text{O}_3$  in sample

$A$  = µg  $\text{O}_3$  after blank correction

$(\mu\text{g/mL NO}_3^-)_b$  = Amount found (from calibration curve) in blank

$(\mu\text{g/mL NO}_3^-)_s$  = Amount found (from calibration curve) in sample

$(\text{Sol Vol})_b$  = Blank solution volume (mL) from Section 3.5.2 (normally 5 mL)

(Sol Vol) <sub>s</sub>	= Sample solution volume (mL) from Section 3.5.2 (normally 5 mL)
CF	= Conversion factor = O <sub>3</sub> /NO <sub>3</sub> <sup>-</sup> = 0.7742
Mol Vol	= Molar volume (L/mol) = 24.45 (25 °C and 760 mmHg)
AV	= Air volume (L)
Mol Wt	= Molecular weight for O <sub>3</sub> = 47.997 (g/mol)

3.8 Add the results of the first and second filters to give one final O<sub>3</sub> concentration. If a significant amount of analyte (>25% of first filter) is found on the back-up (second) filter, breakthrough may have occurred. Report possible breakthrough as a note on the report form.

3.9 Report results to the industrial hygienist as ppm O<sub>3</sub>.

#### 4. Backup Data

This method has been validated for 90-L, 180-min samples taken at a flow rate of 0.5 L/min. The method validation was conducted at different concentration levels near the OSHA TWA PEL of 0.1 ppm O<sub>3</sub>. In addition, 15-min samples were also validated near the OSHA Final Rule STEL of 0.3 ppm. The sampling medium used during the validation consisted of a two-section polystyrene cassette containing two IGFFs. The second IGFF serves as a backup filter. During collection efficiency and breakthrough tests, two separate cassettes containing one IGFF each per sample were used. The IGFFs were prepared as described in Section 2.1.3. The 37-mm GFFs were obtained commercially from Gelman Sciences (Lot no. 130404, Product no. 61652, Type A/E, Ann Arbor, MI).

In addition, a separate experiment of a passive monitor for O<sub>3</sub> was conducted early in the evaluation. The passive monitor (Ogawa & Co., USA, Inc., Pompano Beach, FL) operates on a principle similar to the reaction used for this active sampler. The monitor was tested to determine potential OSHA compliance use.

The validation consisted of the following experiments and discussion:

1. An analysis of 20 spiked samples (7 samples each at 1 and 2 times, and 6 samples at 0.5 times the TWA PEL) to evaluate analytical recovery as desorption efficiency (DE).
2. A sampling and analysis of 22 samples (7 samples each at 1 and 2 times, and 8 samples at 0.5 times the TWA PEL) collected from dynamically generated test atmospheres at 50% RH to determine bias and overall error. Samples at a concentration near the STEL (0.3 ppm) were also taken.
3. A determination of the sampling medium collection efficiency at approximately 2 times the TWA PEL.
4. A determination of potential breakthrough.
5. An evaluation of storage stability at room (20-25 °C temperatures for 26 collected samples).
6. A determination of any significant humidity effects during sampling.
7. A determination of the qualitative and quantitative detection limits.
8. Comparison of sampling methods - impinger vs. treated filter vs. passive monitor (AKI vs. IGFF vs. OPS).
9. Interference study.
10. Shelf-life of the IGFFs.
11. Summary.

A generation system was assembled as shown in Figure 2, and used for all experiments except the analysis, shelf-life study, and detection limit determinations. All samples were analyzed by IC using a UV-VIS detector. All known concentrations of generated test atmospheres were determined using the AKI method for ozone (Ref. 5.2). All sampling tests were conducted using side-by-side IC and AKI samples. These samples were then analyzed using the conditions recommended in their methods.

All results were calculated from concentration vs. response curves and statistically examined for outliers. In addition, the analytical recovery (Section 4.1) and sampling and analysis results (Section 4.2) were tested for homogeneity of variance. Possible outliers were determined using the Treatment of Outliers Test (Ref. 5.15). Homogeneity of variance was determined using Bartlett's test (Ref. 5.16). Statistical evaluation was conducted according to the Inorganic Methods Evaluation Protocol (Ref. 5.17). The overall error (OE) (Ref. 5.17) was calculated using the equation:

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

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

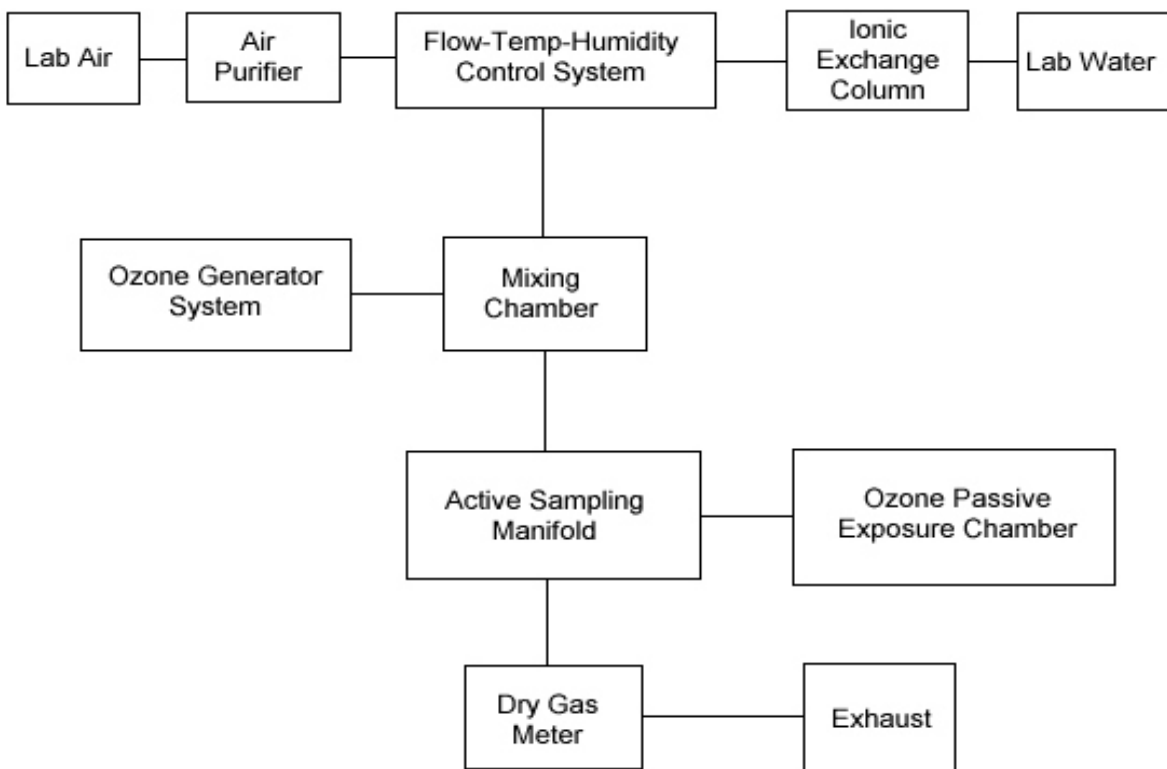


Figure 2

#### 4.1 Analytical Recovery

Ozone oxidizes sodium nitrite to sodium nitrate on the filter. To test the relative analytical capability of this method, sodium nitrate was used as the analytical spike. Twenty samples were prepared by adding known amounts of NO<sub>3</sub><sup>-</sup> (as NaNO<sub>3</sub>) stock solution to the IGFFs to determine desorption efficiencies (DEs) for the analytical portion of the method.

4.1.1 Procedure: Each IGFF was spiked using a 25- or 50-μL syringe (Hamilton Microliter/Gastight Syringe, Hamilton Co., Reno, NV). The IGFF samples were inside cassettes when spiked with aqueous solutions. Spikes were either 11.5, 23.0, and 46.0 ug NO<sub>3</sub><sup>-</sup>. These levels correspond to approximately 0.5, 1, and 2 times the TWA PEL for a

90-L air sample at a 0.5-L/min flow rate. The cassettes were allowed to sit overnight and then analyzed.

4.1.2 Results: Desorption efficiencies are presented in Table 1. As shown, the average DE is very close to 1.0. No DE corrections are necessary for O<sub>3</sub> collection using IGFFs.

Table 1  
Ozone (as NO<sub>3</sub><sup>-</sup>) Analysis - Desorption Efficiency (DE)

level (-)	N	mean DE	SD	CV <sub>1</sub>
0.5 × PEL	6	0.979	0.055	0.056
1 × PEL	7	1.025	0.029	0.028
2 × PEL	7	0.977	0.47	0.048
all levels	20	0.994	-	0.045*

\*CV<sub>1</sub> (pooled)

#### 4.2 Sampling and Analysis

To determine the precision and accuracy of the method, known concentrations of O<sub>3</sub> were generated, samples were collected, and analyzed.

##### 4.2.1 Procedure:

1) Test atmospheres of O<sub>3</sub> were generated using two ozone generators (Model 565, ThermoElectron Instruments, Hopkinton, MA) simultaneously to achieve as high O<sub>3</sub> concentrations as possible. The O<sub>3</sub> gas was diluted with filtered, humidified air using the system shown in Figure 2 and discussed below. A glass mixing chamber was used to facilitate blending of ozone with the diluent air.

2) Dynamic generation system

A Miller-Nelson Research Inc. flow, temperature, and humidity control system (Model HCS-301, Monterey, CA) was used to control and condition the dilution airstream. All generation system fittings and connections were Teflon. The O<sub>3</sub> concentrations were varied by adjusting the dilution airstream Volume. The dilution airstream was adjusted using the mass flow controller of the Miller-Nelson system. For this experiment, the system was set to generate test atmospheres at 50% RH and 25 °C. Test atmosphere concentrations were approximately 0.5, 1, and 2 times the OSHA TWA PEL and at the OSHA STEL.

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

4) IGFF/cassette samples were attached to the Teflon sampling manifold using Gilian Gil-Air SC pumps (Gilian Instrument Corp., W. Caldwell, NJ) to draw the O<sub>3</sub> test atmosphere through the IGFF samples. Pump flow rates were approximately 0.5 and 1.5 L/min and sampling times were 180 and 15 min for TWA and STEL experiments, respectively.

4.2.2 Results: The results are shown in Tables 2a and 2b. The spiked sample (Table 1) and test atmosphere sample (Table 2a) results each passed the Bartlett's test and were pooled to determine a CV<sub>T</sub> for the TWA sampling and analytical method.



Table 2a  
Ozone sampling and Analysis - TWA PEL Determinations

level (-)	N	ave recovery	SD	CV <sub>2</sub>	OE <sub>2</sub> (±%)
0.5	8	1.032	0.060	0.059	14.9
1	7	1.071	0.023	0.022	11.5
2	7	0.937	0.028	0.030	12.3
all levels	22	1.014	-	0.041*	9.7**

\*CV<sub>2</sub> (pooled) - \*\* OE<sub>2</sub> (pooled)

The total pooled coefficients of variation (CV<sub>T</sub>), bias, and total overall error (OE<sub>T</sub>) are as follows:

$$CV_T (\text{pooled}) = 0.045 \quad \text{bias} = + 0.014 \quad OE_T = 10.4\%$$

(Note: The CV<sub>T</sub> and OE<sub>T</sub> values include data from Section 4.1 and are calculated using equations specified in Refs. 5.16-5.17.)

Table 2b  
Ozone Sampling and Analysis - STEL PEL Determination  
(Known O<sub>3</sub> Concentration = 0.33 ppm)

level(-)	N	mean ppm found	SD	CV	recovery	OE
STEL	5	0.325	0.018	0.054	98.5%	±12.3%

#### 4.3 Collection Efficiency

**Procedure:** Seven IGFF/cassettes were used to collect a concentration of approximately 2 times the OSHA TWA PEL for 180 min at 0.5 L/min (50% RH and 25 °C. The amounts of O<sub>3</sub> gas collected on the first and second IGFFs were determined. The collection efficiency (CE) was calculated by dividing the amount of O<sub>3</sub> collected in the first filter by the total amount of O<sub>3</sub> collected in the first and second IGFFs.

**Results:** The results in Table 3 show a CE of 100%. No O<sub>3</sub> was found in the second IGFF for the CE experiment and indicates the IGFFs have adequate collection Of O<sub>3</sub> near the PEL.

Table 3  
Collection Efficiency (CE)  
2 × PEL - 25 °C - 50% RH

sample no.	ppm O <sub>3</sub>		CE, %
	1 <sup>st</sup> IGFF	2 <sup>nd</sup> IGFF	
1	0.209	ND	100.0
2	0.220	ND	100.0
3	0.203	ND	100.0
4	0.216	ND	100.0
5	0.211	ND	100.0
6	0.204	ND	100.0
7	0.206	ND	100.0

Notes: (a) Sampled at 0.5 L/min for 180 min.  
(b) Samples desorbed using a sample solution volume of 5.0 mL  
(c) ND = None detectable (< 0.008 ppm O<sub>3</sub>)

#### 4.4 Breakthrough

(Note: Breakthrough is defined as > 5% loss of analyte from the first IGFF to a backup IGFF at 50% RH)

**Procedure:** The same procedure as the CE experiment (Section 4.3) was used with two exceptions: In addition to the 2 X concentration, the generation concentration was increased to a level approximately 4 times the TWA PEL, and samples were taken at approximately 0.5 L/min for 240

min. Another test was conducted for 6 times the TWA PEL using a sampling rate of approximately 0.25 L/min for 240 min. Due to limitations on the O<sub>3</sub> generators and the generation system, larger O<sub>3</sub> concentrations could not be achieved.

The amount of breakthrough for each sampling cassette was calculated by dividing the amount collected in the second IGFF by the total amount of O<sub>3</sub> collected in the first and second IGFFs.

**Results:** For measurements near the TWA PEL, no breakthrough of O<sub>3</sub> into the second section was found at an approximate concentration of 0.2 ppm O<sub>3</sub> (Table 4a), and indicates the first IGFF has adequate retention of O<sub>3</sub> at 2 times TWA PEL. However, the average breakthrough was 7.5% at an approximate concentration of 0.4 ppm O<sub>3</sub> (Table 4b) for 240 min at 0.5 L/min flow rate. No break-through was found at the approximate concentration of 0.6 ppm O<sub>3</sub> (Table 4c) when using a lower flow rate of 0.25 L/min. For the STEL, no breakthrough was found at approximate concentration of 0.3 ppm O<sub>3</sub> (Table 4d) for 15 min at 1.5 L/min sample collection flow rate.

Table 4a  
Breakthrough Study - 0.5 L/min  
2 × PEL - 25 °C - 50% RH

sample no.	ppm O <sub>3</sub>		Breakthrough, %
	1 <sup>st</sup> IGFF	2 <sup>nd</sup> IGFF	
1	0.242	ND	0
2	0.281	ND	0
3	0.190	ND	0
4	0.227	ND	0
5	0.238	ND	0
6	0.215	ND	0

- Notes:
- (a) Sampled at - 0.5 L/min for 240 min
  - (b) Due to the larger sampling period and thus larger mass collected, the first IGFF was desorbed using larger sample solution volumes of 10.0 mL.
  - (c) ND = None detectable (< 0.008 ppm O<sub>3</sub>)

Table 4b  
Breakthrough Study - 0.5 L/min  
4 × PEL - 25 °C - 50% RH

sample no.	ppm O <sub>3</sub>		CE, %
	1 <sup>st</sup> IGFF	2 <sup>nd</sup> IGFF	
1	0.425	ND	0
2	0.385	ND	0
3	0.395	ND	0
4	0.363	ND	0
5	0.383	ND	0
6	0.342	ND	0

- Notes:
- (a) Sampled at - 0.5 L/min for 240 min
  - (b) Due to the larger sampling period and thus larger mass collected, the first IGFF was desorbed using larger sample solution volumes of 15.0 mL.
- Statistical analysis - N = 8; mean = 7.5; SD = 1.5; CV = 0.20

Table 4c  
Breakthrough Study - 0.25 L/min  
4 × PEL - 25 °C - 50% RH

sample no.	ppm O <sub>3</sub>		Breakthrough, %
	1 <sup>st</sup> IGFF	2 <sup>nd</sup> IGFF	
1	0.563	ND	0
2	0.600	ND	0
3	0.586	ND	0
4	0.661	ND	0
5	0.566	ND	0
6	0.558	ND	0

- Notes:
- (a) Sampled at - 0.25 L/min for 240 min

- (b) Due to the larger sampling period and thus larger mass collected, the first IGFF was desorbed using larger sample solution volumes of 10.0 mL.  
(c) ND = None detectable (<0.008 ppm O<sub>3</sub>)

Table 4d  
Breakthrough Study - 1.5 L/min  
1 × PEL - 25 °C - 50% RH

sample no.	ppm O <sub>3</sub>		Breakthrough, %
	1 <sup>st</sup> IGFF	2 <sup>nd</sup> IGFF	
1	0.440	ND	0
2	0.308	ND	0
3	0.333	ND	0
4	0.346	ND	0
5	0.306	ND	0
6	0.334	ND	0

- Notes: (a) Sampled at - 1.5 L/min for 15 min  
(b) Samples desorbed using a sample solution volume of 5.0 mL  
(c) ND = None detectable (< 0.032 ppm O<sub>3</sub>)

#### 4.5 Storage Stability

**Procedure:** A study was conducted to assess the stability of the NO<sub>2</sub><sup>-</sup> + O<sub>3</sub> reaction product, NO<sub>3</sub><sup>-</sup> on the IGFFs. A room temperature storage stability study using 26 samples taken near the OSHA TWA PEL of 0.1 ppm was performed. All samples were stored under normal laboratory conditions (20-25 °C) in a plastic bag in a drawer. Seven samples were initially desorbed and analyzed; seven more samples were desorbed and analyzed after 5 days, followed by six samples at 15, and 30 days, respectively.

**Results:** The mean of samples analyzed after 30 days was within 10% of the mean of samples analyzed the first day, as shown in Table 5 and Figure 3 below.

Table 5  
Storage Stability - Ozone  
(25 °C, and 50% RH)  
(Known O<sub>3</sub> Concentration = 0.123 ppm)

Day	N	Mean O <sub>3</sub> Found	SD	CV	Recovery (%)
1	7	0.122	0.005	0.038	99.2
5	7	0.120	0.004	0.036	97.6
15	6	0.135	0.002	0.015	109.8
30	6	0.116	0.006	0.052	94.3

# Storage Stability

## Ozone

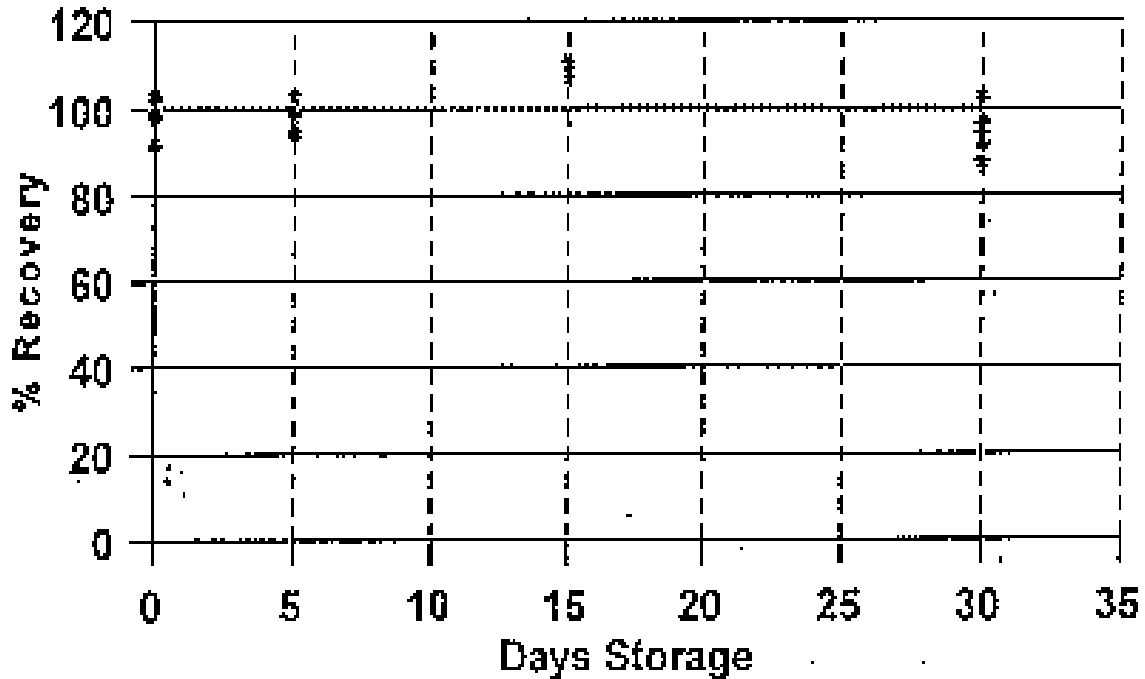


Figure 3

### 4.6 Humidity Study

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

**Results:** Results of the humidity tests are listed in Table 6. An F test was used to determine if any significant effect occurred when sampling at different RHs. As shown, at the 99% confidence level, the calculated F values are much smaller than critical F values (Ref. 5.16) for all the concentrations tested; therefore, no significant difference in results occurred across the RH ranges tested.

Table 6  
Humidity Test - Ozone  
25 °C

Level	RH, %	N	Mean O <sub>3</sub> Found	SD	CV	Taken	Recovery, %	F <sub>crit</sub>	F <sub>calc</sub>
0.5 × PEL	30	7	0.073	0.008	0.107	0.070	104	5.93	0.02
	50	8	0.072	0.004	0.059	0.070	103		
	80	7	0.060	0.001	0.024	0.058	103		
1 × PEL	30	6	0.119	0.007	0.059	0.115	103	6.11	2.62
	50	7	0.118	0.003	0.022	0.110	107		
	80	7	0.101	0.002	0.022	0.098	103		
2 × PEL	30	7	0.174	0.005	0.030	0.172	101	6.01	2.71
	50	7	0.222	0.006	0.028	0.224	99.1		
	80	7	0.231	0.006	0.027	0.237	97.5		

#### 4.7 Qualitative and Quantitative Detection Limit Study

A modification of the National Institute for Occupational Safety and Health (NIOSH) detection limit calculations (Refs. 5.18-5.19) was used to calculate detection limits.

**Procedure:** Low concentration samples were prepared by spiking aqueous standards prepared from NaNO<sub>3</sub> (Section 3.3.4) at five different concentrations on the IGFFs. Samples were analyzed using a 50-μL sample injection loop and a UV-VIS detector setting of 2 AUFS.

**Results:** The IGFF spiked sample results are shown in Table 7 for qualitative and quantitative detection limits, respectively. The qualitative detection limit is 0.37 μg/mL as NO<sub>3</sub><sup>-</sup> at the 99.8% confidence level. The quantitative detection limit is 1.25 ug/mL as NO<sub>3</sub><sup>-</sup>. Using a 90-L air volume and a 5-mL sample solution volume, the qualitative and quantitative detection limits are 0.008 ppm and 0.03 ppm, respectively, as O<sub>3</sub>.

Table 7  
Qualitative and Quantitative Detection Limits (NIOSH Method)

Sample No.	O <sub>3</sub> (as NO <sub>3</sub> <sup>-</sup> ) Level				
	Blank	0.1 μg/mL	0.2 μg/mL	0.5 μg/mL	1.0 μg/mL
	PA	PA	PA	PA	PA
1	2.05	2.73	2.25	3.17	5.87
2	1.98	2.60	3.15	4.15	4.99
3	2.02	1.81*	3.15	3.21	4.98
4	2.03	2.60	3.23	4.09	5.76
5	2.02	2.68	4.55*	4.12	5.81
6	1.74*	2.69	3.79	3.24	5.81

\* Outlier  
PA - Integrated Peak Area (NO<sub>3</sub><sup>-</sup>)/100,000

The average responses of the low-level calibration samples were plotted to obtain the linear regression equation ( $Y = mX + b$ ), and the predicted responses ( $\hat{Y}_i$ ) at each X.

Using the equations:

$$S_y = \sqrt{\frac{\sum (\hat{Y}_i - Y_i)^2}{(N - 2)}}$$

$$Q1 = \frac{3S_y}{m}$$

$$Q2 = (3.33)Q1$$

Therefore,  $Q1 = (3S_y/m = 0.37 \mu\text{g/mL as NO}_3^-$   
 $\Rightarrow 1.85 \mu\text{g as NO}_3^-$  (5-mL sample volume)  
 $\Rightarrow 0.008 \text{ ppm O}_3$  (90-L air volume)

$Q2 = (3.33)Q1$   
 $\Rightarrow 0.027 \text{ ppm O}_3$  (90-L air volume)

where:

B = mean blank response  
 b = intercept of the regression  
 m = analytical sensitivity or slope as calculated by linear regression  
 $S_y$  = standard error of the regression = 0.21667  
 N = number of data points  
 Q1 = qualitative detection limit  
 Q2 = quantitative detection limit

The Correlation Coefficient (r) and Coefficient of Determination ( $r^2$ ) for the above data were  $r = 0.986$  and  $r^2 = 0.972$ .

#### 4.8 Comparison of Sampling Methods

This method was compared with the classical AKI approach and a passive monitor method. The Ogawa passive sampler (OPS), developed by the Harvard School of Public Health (HSPH), was originally designed to sample for nitrogen oxides in the environment. Modifications allowed its use to monitor ambient environmental ozone. The reaction principle and analysis are similar to this IGFF method; however, the impregnating solution is slightly different (and proprietary for the passive system), and the samples are analyzed by IC for nitrate ion using conductivity detection instead of UV-VIS. Prior to using the OPS method for this comparison, the sampling rate was examined. Due to face velocity dependence, sampling rates are critical to the performance of the passive monitor during this comparison. The determination of sampling rate is detailed in the Appendix.

Procedure: In order to compare performance, the IGFF/cassettes (this study), AKI samples, and OPSs were collected side by side from the generation system at approximately 0.5, 1 and 2 times the PEL. The IGFF/cassettes and OPSs were analyzed by IC. The AKI samples were analyzed by a colorimetric procedure further described in Ref. 5.2. The average sampling rate as determined by SLTC for the face velocity achieved, 21.93 cm<sup>3</sup>/min, was used for OPSs.

Results: Table 8 shows the results of the comparison study. As shown, the IGFF/cassettes, the AKI samples, and OPSs are in good agreement except that OPSs are slightly higher for 1 times and lower for 2 times PEL.

Table 8  
 Comparison of Methods (Summary)  
 (25 °C and 50% RH)

Set #	Method	O <sub>3</sub> Found, ppm	N	SD	CV
1	AKI	0.070	3	0.006	0.086
	IGFF	0.072	8	0.004	0.056
	OPS	0.073	4	0.003	0.041
2	AKI	0.110	3	0.002	0.018
	IGFF	0.118	7	0.003	0.025
	OPS	0.129	7	0.017	0.132
3	AKI	0.224	3	0.008	0.036
	IGFF	0.210	7	0.006	0.029
	OPS	0.187	7	0.012	0.064

where: AKI Alkaline potassium iodide (Ref. 5.2)  
 IGFF Impregnated glass fiber filter (this study)  
 OPS Ogawa passive sample for ozone (Refs. 5.10 and 5.20)

NOTE: Although the passive monitor performed reasonably well during the comparison, detection limit calculations indicate potential problems may be incurred for OSHA compliance use. The monitor was originally designed for environmental (24-h) use. Using the manufacturer's stated detection limit of 200 ppb-h as analyzed using IC and a conductivity detector (the manufacturer's recommended analytical technique), an 8-h detection limit of 0.025 ppm would be obtained (using a UV-VIS detector SLTC indicates a quantitative detection limit of about 0.1 ppm-h; however, for STEL or intermittent sampling the monitor still appears not sufficiently sensitive). This would necessitate 7- to 8-h sampling and would not be conducive to STEL or intermittent sampling occasionally required in monitoring situations. The monitor appears beneficial in industrial hygiene situations provided large concentrations (> 0.1 to 0.2 ppm O<sub>3</sub>) are present or 7- to 8-h sampling is performed. The study to determine applicability was halted after preliminary determinations indicated the passive monitor also suffered from the same negative interference from SO<sub>2</sub> as the active sampler (Section 4.9). In a recent paper (Ref. 5.10), the authors indicated that SO<sub>2</sub> should not interfere with the passive sampler collection of O<sub>3</sub>; however, experiments to verify this were not presented in the paper.

#### 4.9 Interference Study

As previously discussed in Section 1., oxidizing gases have interfered with the determination of O<sub>3</sub> in previous methods (Refs. 5.1-5.2, 5.4). Several tests were conducted to evaluate any possible interference from NO<sub>2</sub> or SO<sub>2</sub>.

Procedure: Possible interferences from NO<sub>2</sub> and SO<sub>2</sub> were tested using several sets of IGFF/cassette samples. A test was conducted by taking four samples at approximately 6 ppm NO<sub>2</sub> and compared to four samples without NO<sub>2</sub> which served as "control" samples. Several tests were conducted to evaluate any SO<sub>2</sub> interference by comparing results of six samples with SO<sub>2</sub> to another four to six samples without SO<sub>2</sub>, present. These tests included two different SO<sub>2</sub> concentrations and use of oxidizer tubes for removal of SO<sub>2</sub> from the sampled air prior to O<sub>3</sub> reaction with the treated filters.

Two different kinds of oxidizer tubes were evaluated. Both were manufactured by SKC Inc. (Eighty Four, PA) and are used to convert nitric oxide (NO) to nitrogen dioxide (NO<sub>2</sub>) during sampling for NO. The two types of oxidizer tubes are:

<u>Tube Label</u>	<u>Substrate</u>	<u>Abbrev.</u>
Oxidizer Special	Chromate impregnated sand	OS
Misc-Spec	Chromate impregnated material (Composition of substrate unknown)	MS

Both tube labels are designations given by SKC. Chromate impregnated sorbent has been shown to effectively remove SO<sub>2</sub> during ozone sampling (Ref. 5.21). All samples were taken at a flow rate of about 0.5 L/min for 180 min. The generation system concentration was approximately 1.5 times the TWA PEL for ozone.

Results: Table 9 shows the results of the IGFF/cassette sample sets:

Sample Set No.	Description
1)	O <sub>3</sub> with and without NO <sub>2</sub>
2)	O <sub>3</sub> with and without SO <sub>2</sub> (3.41 ppm)
3)	O <sub>3</sub> with and without SO <sub>2</sub> (1.06 ppm)
4)	O <sub>3</sub> with and without SO <sub>2</sub> (0.35 ppm)
5)	O <sub>3</sub> + SO <sub>2</sub> with and without OS oxidizer
6)	O <sub>3</sub> + SO <sub>2</sub> with OS oxidizer before and after conditioning
7)	O <sub>3</sub> + SO <sub>2</sub> with and without MS oxidizer
8)	O <sub>3</sub> + SO <sub>2</sub> with MS oxidizer before and after conditioning
9)	Comparison study between 50% and 80% RH for O <sub>3</sub> +SO <sub>2</sub> with MS oxidizer after conditioning.

Note: Oxidizer tube conditioning is based on the procedure discussed in Section 2.

Table 9  
Interference Study - Ozone  
(25 °C - 50% RH and 1.5 ×PEL)

Sample Set #	Interferant Conc'n, ppm	Oxidizer (Yes or No)	Conditioning (Yes or No)	N #	Mean O <sub>3</sub> , ppm	SD O <sub>3</sub> , ppm	CV%
1	NO <sub>2</sub> , 6.38	No	NA	4	0.129	0.007	5.5
	NO <sub>2</sub> , 0	NA	NA	4	0.134	0.003	20.
2	SO <sub>2</sub> , 3.41	No	NA	6	ND	-	-
	SO <sub>2</sub> , 0	NA	NA	6	0.168	0.009	5.5
3	SO <sub>2</sub> , 1.06	No	NA	6	ND	-	-
	SO <sub>2</sub> , 0	NA	NA	6	0.169	0.013	7.8
4	SO <sub>2</sub> , 0.35	No	NA	6	ND	-	-
	SO <sub>2</sub> , 0	NA	NA	6	0.169	0.013	7.8
5	SO <sub>2</sub> , 1.06	Yes	Yes	6	0.141	0.009	6.3
	SO <sub>2</sub> , 0	NA	NA	6	0.142	0.009	6.0
6	SO <sub>2</sub> , 1.06	Yes	No	6	0.108	0.012	10.7
	SO <sub>2</sub> , 1.06	Yes	NA	6	0.141	0.009	6.3
7	SO <sub>2</sub> , 1.06	Yes	Yes	6	0.153	0.005	3.1
	SO <sub>2</sub> , 0	NA	NA	4	0.154	0.001	0.9
8	SO <sub>2</sub> , 1.06	Yes	No	6	0.141	0.014	9.6
	SO <sub>2</sub> , 1.06	Yes	NA	6	0.153	0.005	3.1
9	SO <sub>2</sub> , 1.06	Yes	Yes	6	0.153	0.005	3.1
	SO <sub>2</sub> , 1.06*	Yes	Yes	5	0.145	0.008	5.8

\* 80% RH was used instead of 50%

- Notes: (a) NA = Not applicable  
 (b) ND = None detectable (< 0.008 ppm O<sub>3</sub>)  
 (c) Flow Rate = 0.5 L/min  
 (d) Sample Solution Volume for Desorption = 5.0 mL  
 (e) All oxidizers were conditioned for 4 h at a concentration of approximately 0.1 ppm O<sub>3</sub>

As shown in Sample Set #1, 6.38 ppm NO<sub>2</sub> caused no interference when sampling at 1.5 times TWA PEL ozone. When SO<sub>2</sub> is present along with ozone, a negative interference equal to 100% of an equimolar concentration of ozone is noted as shown in Sample Sets #2, #3 and #4. Sample Sets #5 and #7 show no interference occurs when using the oxidizer tubes. Sample Sets #6 and #8 show the difference in recovery when using conditioned and unconditioned oxidizer tubes. As shown, the oxidizer gave results about 23% lower when it was not conditioned (0.108 vs. 0.141 ppm O<sub>3</sub> when conditioned). Although, the recoveries improved for the MS oxidizer without conditioning (0.141 vs. 0.153 ppm when conditioned), they were still low and it is recommended to passivate either type of oxidizer tube. Sample Set #9 shows no significant difference in O<sub>3</sub> recovery when SO<sub>2</sub> is present at 50% and 80% RH.

An additional test was conducted to determine if the passive monitor would be adversely affected by SO<sub>2</sub> in a similar fashion as the active sampler. Side-by-side active and passive samples were taken while varying the amount of SO<sub>2</sub>. Both passive and active samples were prepared using the procedure stated in this method for IGFFs. (Section 2.1) Additional passive samplers were also purchased from Ogawa; the procedure, type, and amount of chemicals used in their treatment preparation is unknown.

As shown in Table 10, the passive monitor, regardless of treatment in-house or from Ogawa, appears to display the same SO<sub>2</sub> interference as the active sampler. Detection limits are similar to what is stated earlier for both active and passive samplers.



Table 10  
Active vs. Passive Sampler - SO<sub>2</sub> Interference

Sample Set #	Active or Passive	Interferant, SO <sub>2</sub> Conc (ppm)	N #	Mean O <sub>3</sub> , ppm	SD O <sub>3</sub> , ppm	CV %
1	Active	0	4	0.164	0.006	3.5
1	Active	1.89	3	ND	-	-
1	Passive	0	6	0.167	0.017	10.1
1	Passive	1.89	6	ND	-	-
2	Active	0	2	0.132	0.007	0.5
2	Active	1.89	3	ND	-	-
2	Passive	0	6	0.130	0.012	9.0
2	Passive	1.89	6	ND	-	-

Note: N = number of samples taken.  
 Sample Set #1 represents passive samplers prepared using 13-mm glass fiber filters prepared as stated in Section 2.1  
 Sample Set #2 represents passive samplers purchased from Ogawa.  
 Sets 1 and 2 used identical Ogawa sample holders.

#### 4.10 Shelf Life of the IGFFs

Thirty-nine IGFFs were prepared according to the procedure described in Section 2.1.3 to determine the potential shelf-life of the nitrite-impregnated filters. Previous reports indicate the Ogawa passive monitors have a conservative shelf-life due to aging of four weeks. The manufacturer indicates an 8-week life-span can be used if necessary and appropriate blank corrections are performed. The aging, or eventual conversion to nitrate appears to be facilitated by oxygen and small amounts of ozone in the atmosphere. The passive monitors use a reaction principle similar to the active sampling filters in this method. For this active sampling method, the extent of nitrite conversion to nitrate on stored filters was used to indicate stability and was measured over a period of up to 58 days.

Procedure: Four tests were conducted to assess IGFF shelf life:

- Set 1) The first test was performed using 15 IGFFs which were stored in a clean and sealed plastic bag after preparation. Five IGFFs were initially taken and served as "control" IGFFs, desorbed with DI H<sub>2</sub>O and analyzed for total nitrite using peak area; then six IGFFs were desorbed and analyzed after 22 days; finally, the remaining four IGFFs were desorbed and analyzed after a 45-day storage.
- Set 2) A second test was conducted with ten more filters; six were analyzed after 6 days, and four filters analyzed after 28 days.
- Set 3) A third test was performed using 11 IGFFs which were placed in cassettes. The cassettes were then sealed with gel bands and plastic plugs, and stored in a clean and sealed plastic bag after preparation.
- Set 4) This set of four filters was prepared similar to the third set; however, this set was used to assess ability to collect samples after storage. Three of the IGFF/cassettes were used to collect O<sub>3</sub> vapor (0.15 ppm O<sub>3</sub>) after 58 days of storage.

Results: Results are listed in Table 11 and further discussed below:

- Set 1) The conversion of nitrite to nitrate does not significantly occur under the storage conditions specified above for a period of approximately 20-30 days. After 45 days, conversion appears evident. The mean peak area of the IGFFs analyzed after 22 days was only a 9% increase over the Day 0 value and almost a 50% increase after a 45-day storage.
- Set 2) The mean of the IGFFs analyzed after 28 days was only a 2% increase over the value of Day 6.

Set 3) The mean of the IGFFs analyzed after 57 days was a 23% increase over the value of Day 0.

Set 4) After blank correction and 58-day storage, the mean recovery of the O<sub>3</sub> collected was 95.5%. Mean O<sub>3</sub> found was 0.143 ppm after blank IGFF correction, and 4.0% CV.

Table 11  
Shelf-Life Test of IGFF

Sample Set #	Day i	N #	Mean* ×10 <sup>5</sup>	SD ×10 <sup>5</sup>	CV %	Ratio X <sub>i</sub> /X <sub>0</sub>
1	0	5	2.02	0.025	1.3	1.00
	22	6	2.20	0.080	3.7	1.09
	45	4	2.93	0.100	3.5	1.45
2	6	6	2.33	0.200	8.6	1.00
	28	4	2.37	0.091	3.8	1.02
3**	0	6	4.71	0.740	15.7	1.00
	57	5	5.30	1.180	22.2	1.23

\* Peak area.

X<sub>i</sub>/X<sub>0</sub> Ratio of IGFFs (mean peak area of Day 1 compared to that of mean Day 0).

\*\* IGFFs were placed and stored in cassettes, sealed with scaling bands and plastic plugs.

#### 4.11 Summary

The validation results indicate the method meets both the OSHA criteria for accuracy and precision (Ref. 5.17). The performance during collection efficiency, storage stability, and humidity tests is adequate. For the breakthrough study, it appears that 7.5% breakthrough occurs onto a second IGFF at a concentration of 0.4 ppm O<sub>3</sub> at 0.5 L/min for 240 min. Although the second filter effectively captures the analyte at 0.4 ppm, precautions should be taken at higher concentrations. For O<sub>3</sub> concentrations above 0.4 ppm, a flow rate of 0.25 L/min can be used. Breakthrough is not evident at lower concentrations; however, the second IGFF should always be analyzed to assure capture of all analyte. Experiments above approximately 0.6 ppm using a sample collection rate of 0.25 L/min were not performed due to limitations in the test atmosphere generation system. Detection limits (as NO<sub>3</sub><sup>-</sup>) are adequate when samples are taken for 180 min at 0.5 L/min. The conversion of nitrite on the IGFFs appears limited up to 28 days after impregnating if the 2 treated filters are stored in a clean, sealed plastic bag.

The mechanism of the SO<sub>2</sub>/O<sub>3</sub> interference which diminishes the O<sub>3</sub> conversion of nitrite to nitrate is unknown. Using the AED-030 (semiconductor sensor) direct-reading instrument side-by-side with the IGFFs while sampling an SO<sub>2</sub>/O<sub>3</sub> atmosphere, a corresponding loss of O<sub>3</sub> was not noted. The ability of glass fiber filters to capture and convert SO<sub>2</sub>, due primarily to their slightly basic nature, was previously noted in OSHA Method ID-200 for sulfur dioxide. It has been reported in the literature (Ref. 5.22) that the chemistry of SO<sub>2</sub> in ambient air and on surfaces is complex. Fortunately, an oxidizer tube appears to completely remove SO<sub>2</sub> from the sampled stream. Presumably the SO<sub>2</sub> can react with any ozone or oxygen in the presence of nitrite (and possibly glass fiber filters) to form sulfite and eventually sulfate. No significant increase in the sulfate content over background amounts was noted in the chromatograms of IGFF samples taken after using oxidizer tubes to sample an SO<sub>2</sub>/O<sub>3</sub> atmosphere. For samples taken in the SO<sub>2</sub>/O<sub>3</sub> atmosphere without oxidizer tubes, a significant increase in sulfate content was noted from the resultant oxidation of SO<sub>2</sub>. The SO<sub>2</sub> interference appears to be a sampling phenomena occurring at the surface of the IGFFs and is not dependent on analysis. Other environmental pollutants which could potentially adversely affect this ozone sampling method have been considered in the literature. For example, nitric acid vapor, if present, could be collected on the IGFFs during sampling. However, under typical ambient conditions this positive interference probably represents less than 5% of the nitrate formed during the nitrite/ozone reaction (Ref. 5.23). Further study may be needed to determine other oxidized or reduced compounds which may coexist with O<sub>3</sub> and cause either positive or negative interferences, such as peroxyacetyl nitrate (PAN), a strong oxidant, which could oxidize nitrite to nitrate. Since ambient concentrations of PAN are typically 10-20 times smaller than ozone concentrations, significant interference in most locations is not expected (Ref. 5.24).

This method was validated using a UV-VIS detector. A conductivity detector was used to assess potential interference byproducts such as sulfite/sulfate concentrations. Prior to completion of the method another chemist was given approximately 25 field samples to analyze and indicate any problems that may occur during routine analysis. Sample concentrations covered a wide range and were analyzed both by UV and conductivity detection. A difference in ozone results was not noted between the two detectors. Either detector should have adequate sensitivity and capability. The IC conductivity detector has been used for nitrate determination since its inception over 15 years ago. The UV detection technique may be less prone to interferences because of the greater selectivity (wavelength specificity) for each analyte. More crucial to analysis is the ability to separate the nitrite and nitrate peaks using appropriate columns. Precautions should be taken to assure adequate separation prior to sample analysis regardless of which detector is used.

## 5. References

- 5.1 U.S. Environmental Protection Agency: Evaluation of 1 Percent Neutral Buffered *Potassium Iodide Procedure for Calibration of Ozone Monitors* by M. E. Beard, J. H. Margeson, and E. C. Ellis (EPA-600/4-77-005). Environmental Monitoring Series. Research Triangle Park. N.C., 1977.
- 5.2 National Institute for Occupational Safety and Health: Documentation of the NIOSH *Validation Tests* by D. Taylor, R. Kupel and ". Bryant (DHEW-NIOSH publication No. 77-185). NIOSH Analytical Methods for Standard Completion Program (Method No. S8 - Ozone). Washington, D.C.: U.S. Government Printing Office, 1977.
- 5.3 Hekmat, M., P. Fung, and R. Smith: Instability of Ozone Samples Collected in Alkaline Potassium Iodide Solution. *Am Ind. Hyg. Assoc. J.* 53: 672 (1992).
- 5.4 Occupational Safety and Health Administration Salt Lake Technical Center: Ozone (*KIBRT*) in *Workplace Atmospheres* (USDOL/OSHA-SLCAL Method No. ID-150). Salt Lake City, UT: Occupational Safety and Health Administration Salt Lake Technical Center, 1984.
- 5.5 Occupational Safety and Health Administration Salt Lake Technical Center: Ozone (*Stilbene*) in *Workplace Atmospheres* (USDOL/OSHA-SLCAL Method No. ID-209). Salt Lake City, UT: Occupational Safety and Health Administration Salt Lake Technical Center, 1990 unpublished.
- 5.6 Sawatari, K.: Personal Dosimeter for Ozone using the Ozonolysis of Trans-stilbene. *Industrial Health* 22: 117-126 (1984).
- 5.7 Ku, J.C.: *Private Notes*, 1989.
- 5.8 Analytical Instrumental Development Inc.: Ozone Portable Analyzer. Model 560, *Technical Document*. Avondale, PA: Analytical Instrumental Development Inc., 1980.
- 5.9 In USA Inc.: *Ozone Hunter, AET - 030. Technical Document*. Newtonville, MA: In USA Inc., 1992.
- 5.10 Koutrakis, P., J.M. Wolfson, A. Bunyaviroch, S.E. Froehlich, K. Hirano and J.D. Mulik: Measurement of Ambient Ozone Using a Nitrite-Coated Filter. *Anal. Chem.* 65: 209-214(1993).
- 5.11 Hawley, G.G.: *The Condensed Chemical Dictionary*. 11th ed. New York: Van Nostrand Reinhold Co., 1987.
- 5.12 American Society for Testing and Materials (ASTM): *Standard Practice for Safety and Health Requirements Relating to Occupational Exposure to Ozone (E591-80)*. In 1988 Annual Book of ASTM Standards, Section H, Volume 11.03, Philadelphia, PA: ASTM, 1988. pp. 411-439.
- 5.13 "Ozone" Federal Register 54:12 (19 Jan. 1989). pp. 2519-2520.

- 5.14 Occupational Safety and Health Administration Salt Lake Technical Center: *Ion Chromatography Standard Operating Procedure* (Ion Chromatographic Committee). Salt Lake City, UT: Occupational Safety and Health Administration Salt Lake Technical Center, in progress.
- 5.15 Mandel, J.: Accuracy and Precision, Evaluation and Interpretation of Analytical Results, The Treatment of Outliers. In *Treatise On Analytical Chemistry*. 2nd ed., Vol. 1, edited by I. M. Kolthoff and P. J. Elving. New York, NY: John Wiley and Sons, 1978. pp. 282-285.
- 5.16 National Institute for Occupational Safety and Health: *Documentation of the NIOSH Validation Tests* by D. Taylor, R. Kupel, and J. Bryant (DHEW/NIOSH Pub. No. 77-185). Cincinnati, OH: National Institute for Occupational Safety and Health, 1977. pp. 1-12.
- 5.17 Occupational Safety and Health Administration Salt Lake Technical Center: Evaluation Guidelines of the Inorganic Methods Branch. In *OSHA Analytical Methods Manual*. 2nd ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists, 1991. pp. 118.
- 5.18 Burkart, J.A.: General Procedures for Limit of Detection Calculations in the Industrial Hygiene Chemistry Laboratory. *Appl. Ind. Hyg.* 1: 153-155 (1986).
- 5.19 National Institute for Occupational Safety and Health: *Standard Operating Procedures for Industrial Hygiene Sampling and Chemical Analysis, SOP 018*, Cincinnati, OH: National Institute for Occupational Safety and Health, Revised Sept., 1992.
- 5.20 Ogawa & Co., USA, Inc.: *The Ogawa Passive Sampler for Ozone Operation Manual*. Pompano Beach, FL: Ogawa & Co., USA, Inc., 1993.
- 5.21 Committee on Medical and Biologic Effects of Environmental Pollutants: *Ozone and Other Photochemical Oxidants*. National Academy of Sciences, Washington, D.C., 1977. p. 264.
- 5.22 Chang, D.P.Y.: Sulfur Compounds ' in Ambient Environments and Their Simulation in the Laboratory. *Generation of Aerosols and Facilities for Exposure Experiments* edited by K.Willeke. Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1980. p. 302-304.
- 5.23 Koutrakis, P., P. Mueller: Paper No. 89-71.4. In Proceedings of the 82nd Annual Meeting of the Air and Waste Management Association, 1989.
- 5.24 Finlayson-Pitts, B. and J.N. Pitts: *Atmospheric Chemistry*, New York, NY: John Wiley & Sons, 1986.

## Appendix

### Sampling Rate - Ogawa Passive Samplers for Ozone

The OSHA-SLTC was interested in examining performance of the passive monitor for potential OSHA compliance use. The sampling simplicity of the monitor is very attractive to compliance officers, and the possibility of offering both active and passive samplers for O<sub>3</sub> was explored. To verify the passive monitor sampling rate, the mass collected by the passive sampler when exposed to various concentrations of ozone was measured.

Procedure: A "known" concentration was determined from the IGFF method and confirmed by the AKI method. The OPSs, IGFFs, and AKI samples were collected side-by-side from the generation system at approximately 0.5, 1, and 2 times PEL. The passive monitors were placed in a 1-L buret (area section = 19.63 cm<sup>2</sup> or 0.021 ft<sup>2</sup>), and the open end of the buret was sealed with a cork stopper. This exposure chamber was in series with a Teflon sampling manifold where the active samplers were collected. The face velocity (air movement in front of the passive monitor) was 8.3 ft/min. The low face velocity was necessary due to dependence on the generation system design and concentrations generated. The sampling rate must be determined if this face velocity is used in method comparisons. The manufacturer's stated rate of 18.1 cm<sup>3</sup>/min is for higher face velocities. Normal face velocities in general industry typically range from 25 to 100

ft/min. The sampling time was 480 min. Sampling for the passive monitors was conducted according to the OPS instruction manual (Ref. 5.20).

**Results:** The Table below shows the calculated sampling rates at the different O<sub>3</sub> concentrations. The sampling rate was calculated based on diffusion theory. A more detailed description about diffusion theory (Fick's First Law of Diffusion) and specific application can be found elsewhere (e.g., Ref. 5.10). As shown, the average sampling rate is 21.93 ± 2.28 cm<sup>3</sup>/min. Note that this rate lies between the theoretically predicted rate, 24.5 cm<sup>3</sup>/min and the observed value, 18.1 ± 1.9 cm<sup>3</sup>/min reported by HSPH (Ref. 5.10).

Sampling Rate Validation for Ogawa Ozone Passive Samplers  
(25 °C - 50% RH - 8.3 ft/min Face Velocity\* and 480-min Sampling Time)

Level	O <sub>3</sub> Conc ppm	Mean O <sub>3</sub> Mass Found, µg	N #	Mean Sampling Rate**, cm <sup>3</sup> /min	SD cm <sup>3</sup> /min	CV %
0.5 × PEL	0.072	1.507	4	22.22	0.95	4.3
1 × PEL	0.118	2.676	7	24.06	3.39	14.1
2 × PEL	0.210	3.864	7	19.52	1.33	6.8

Average Sampling Rate = 21.93 ± 2.28 cm<sup>3</sup>/min

\* Calculated from 1-L buret used as an exposure chamber (area section = 19.63 cm<sup>2</sup> or 0.021 ft<sup>2</sup>) and test atmosphere flow rate of 5 L/min through the chamber.

\*\* Values calculated based on the following equation:

$$\text{Sampling Rate } \left( \frac{\text{cc}}{\text{min}} \right) = \frac{\text{O}_3 \text{ found } (\mu\text{g}) \times 24.46 \times 1000}{\text{O}_3 \text{ Conc (ppm)} \times 47.997 \times \text{Sampling time (min)}}$$

where: O<sub>3</sub> found (ug) = ug/mL, NO<sub>3</sub> × sampling volume, mL X GF

O<sub>3</sub> found (ug) = ug/mL, NO<sub>3</sub> × 1.9355\*\*\*

\*\*\*If sampling volume = 2.5 mL and GF = Gravimetric factor = 48/62 = 0.7742 are used

24.46 = Molar volume at 25 °C and 760 mmHg

47.997 = Molecular weight of ozone