VOLATILE ORGANIC COMPOUNDS IN AIR

Method No.: PV2120

Control No.: T-PV2120-01-0305-ACT

Matrix: Air

Procedure: A sample is collected by drawing air through an orifice into an evacuated fused silica-lined stainless steel canister. The canisters are analyzed in the laboratory, where they are first pressurized. Aliquots of the air sample are withdrawn, cryofocused, and analyzed by gas chromatography/mass spectrometry to determine the concentrations of compounds collected.

Recommended sampling volume and sampling time: The canister volume is approximately 400 mL. Short-term sampling orifices allow the canister to be filled in less than one minute. Long-term area samples or personal air samples may be collected up to 8 hours or longer.

Detection Limits: Detection and reliable quantitation limits will vary with analyte response factor. Detection limits of low ppb levels are possible for most common analytes.

Status of method: Partially Validated. This method has been subjected to the established evaluation procedures of the SLTC Methods Development Team.

Date: May, 2003

Chemist: Patrick Hearty

1. General Discussion
1.1 Background and History

Evacuated stainless steel canisters with electro-polished inner surfaces, called SUMMA canisters, are widely used in EPA applications when sampling for volatile organic compounds (VOCs) in the environment (1). Canisters have been evaluated for use with a range of volatile organics, including aliphatic and aromatic hydrocarbons, and chlorinated compounds (2). This technique has also been applied to a variety of practical applications, such as indoor air quality problems (3), and other situations involving low levels of volatile contaminants, including the docking of the Russian Priroda module with Space Station Mir (4). The evacuated canisters offer a number of advantages, including elimination of the need for a sampling pump, avoidance of questions concerning sorbent tube collection and recovery, and the ability to make replicate injections and dilutions during analysis.

The development of a process which coats stainless steel with fused silica has led to important advances in chemical sampling and analysis. This material offers the structural strength and impermeability of steel combined with the inertness of fused silica. Entech, Inc., Simi Valley, CA, has combined the fused silica coating with the polished canister technology in a smaller MiniCan, 400-mL capacity, for use as a personal sampler in industrial hygiene. This new technique is leading to improved analytical methods for a variety of reactive and labile compounds of interest at very low levels (5, 6).
Short-term area samples are collected by attaching a sampling orifice to the inlet of the MiniCan. Sampling begins immediately, and is completed when the pressure inside the canister is equal to the atmospheric pressure on the outside, or when the sampling orifice is detached from the canister. For personal air samples, a MiniCan is mounted in a holster attached to a belt fastened around the waist of the worker. A sampling orifice with regulator is attached to the inlet of the canister, and a length of inert tubing leading from the breathing zone of the worker is connected to the inlet of the orifice. In the laboratory, the canister is pressurized with nitrogen, and the contents are analyzed by gas chromatography/mass spectrometry.

The data presented in this method were produced during an evaluation study conducted at OSHA's Salt Lake Technical Center (7).

1.2 Limit Defining Parameters.

1.2.1 Detection Limits

Standards of \( n \)-hexane (5.3 ppb), tetrachloroethylene (5.2 ppb), toluene (5.3 ppb), and \( p \)-xylene (5.3 ppb) were analyzed for determination of detection limits. Lower limits of detection are estimated to be: 0.2 ppb for \( n \)-hexane, 0.4 ppb for tetrachloroethylene, 1 ppb for toluene, and 4 ppb for \( p \)-xylene. (Section 4.1)

1.2.2 Minimum Injection Volume

Using canisters spiked with standards of 50 ppb of the four analytes listed above, injection volumes from 5 mL to 200 mL were analyzed. Results indicate that a 10 mL injection is the smallest volume which provides acceptable precision. (Section 4.2)

1.2.3 Storage Stability

Canisters spiked with each of the four test compounds at 25 ppb were stored at room temperature for up to 14 days. The average of four replicates was as follows: \( n \)-hexane 125%; toluene 97.4%; tetrachloroethylene 89.7%; \( p \)-xylene 100%. (Section 4.3)

To test recovery at higher levels, a single test was run by spiking one canister with trichloroethane at 100 ppm. The measured value after 5 days was 102%.

The draft NIOSH method for canister sampling of VOC's indicates 30-day sample stability for most compounds (8). Some compounds have been reported stable for up to 4 months (2).

1.2.4 Precision

Five canister replicates were spiked with the four test analytes each at a level of 50 ppb. The coefficients of variation for the four analytes were as follows: \( n \)-hexane 13.4%; toluene 6.7%; tetrachloroethylene 7.3%; \( p \)-xylene 6.8%. Data were taken from Table 4.2. Statistical analyses may be found in Tables 4.4.1 through 4.4.4.

1.3 Advantages

1.3.1 Problems with collection efficiency and analyte recovery, which may be encountered with sorbents or filters, are avoided. Evacuated canister sampling is a whole-air sampling technique.

1.3.2 When collecting short-term samples, no sampling error is associated with this method.

1.3.3 Sampling pumps are not needed.

2. Sampling Procedure

2.1 Apparatus

2.1.1 Entech Minicans, 400-mL volume (Entech P/N 29-MC400), were used in this study. Sampling canisters may be obtained from a contract laboratory, and returned to the contract lab after samples are collected. Canisters obtained from the contract lab will be certified clean (9).
2.1.2 Samples are collected by filling evacuated canisters through a sampling orifice. Orifices are available which provide practically instant grab sampling (Entech P/N 39-QFS). Pressure regulated orifices (Entech P/N CS1200E) offer sampling times as short as 2 minutes, or as long as 8 hours or more. These sapphire orifices are said to provide superior flow stability, compared to needle valve or frit-regulated controllers.

2.1.3 For personal sampling, a holster and belt (Entech P/N 39-35000) can be used to attach the canister to the waist of an employee. An inert inlet line (Entech P/N 39-36010) is used to draw air from the employee's breathing zone.
2.1.3 Minican with pressure regulated orifice and personal sampling belt and inlet line.

2.1.4 End caps are removed from the canisters prior to attachment of the sampling regulators, and replaced when sampling is complete.

2.2 Reagents

None needed.

2.3 Sampling Technique

2.3.1 Choose the time-release regulator, either short- or long-term, appropriate for the desired application.

2.3.2 Holding the sampling regulator in one hand, slide back the knurled collar with thumb and index finger.

2.3.3 Hold the canister in the other hand, with protective end cap removed, and with tip of canister facing sampling regulator.

2.3.4 Insert the canister tip into the regulator, and release the knurled collar. No gap should be observable between the regulator and the fitting at the end of the canister.

2.3.5 Sampling begins immediately. (Note the time of day.)

2.3.6 Bear in mind that this is a whole air sampling technique. Lack of selectivity is inherent in this method. If for example, the person performing the sampling, or the person being sampled should be wearing perfume or cologne, volatile components of these will also be sampled.

2.3.7 When sampling is complete, reverse above steps to disengage the canister from the regulator. Slide back the knurled collar with thumb and index finger, and separate the canister from the regulator. Release the knurled collar.
2.3.8 Replace the protective end cap onto the canister, and seal each canister with an OSHA Form 21.

2.3.9 Record sampling time. (Note the time of day when sampling is completed.)

2.3.10 No sample blank is necessary if the canisters were assured to be clean at the outset of sampling. A sample collected in a control area may be included if desired.

2.4 Safety Precautions (sampling)
2.4.1 Follow all safety procedures which apply in the work area being sampled.

2.4.2 If personal sampling is being conducted, attach sampling equipment to the employees in such a manner that it will not interfere with work performance or safety.

3. Analytical Procedure

It is possible to conduct sampling using this method even if your laboratory is not equipped with apparatus for cleaning and analysis of canister samples. Contract laboratories will provide loan of cleaned and evacuated canisters followed by GC/MS analysis of your samples (9).

3.1 Apparatus
3.1.1 Entech Canister System consisting of a Model 7032L 21-Position Loop Autosampler and Model 7100 Preconcentrator, connected to a GC/mass spectrometer system. A Hewlett-Packard 5973 GC/mass spectrometer was used in this evaluation.

3.1.2 Entech Model 4600 Dynamic Dilution System.

3.1.3 Entech Model 3100 Canister Cleaning System.

3.1.4 Summa Canisters 6-liter volume, Silonite coated.

3.1.5 A GC column capable of providing adequate separation of the analytes of interest must be chosen. A 30-m DB-1-MS column, 0.32-mm i.d. with df 0.25 microns (J&W Scientific, catalog #1230132) was used in this study.

3.2 Reagents
3.2.1 Standard gas mixture according to the compounds to be analyzed.

3.2.2 Liquid nitrogen.

3.2.3 Helium (ulta high purity).

3.3 Canister Cleaning
3.3.1 The Entech Model 3100 is used to clean canisters prior to sampling. Canisters are evacuated to 13 kPa (2 psi), then filled with clean, humidified nitrogen to 172 kPa (25 psi), while heated to 80°C.

3.3.2 This process is repeated until no residual contaminants remain. Canisters are pressurized to 207 kPa (30 psi) with nitrogen, and an aliquot is withdrawn for analysis (Section 3.6) to ascertain cleanliness.

3.3.3 Canisters which are to be used to sample relatively high (ppm) concentrations of analytes are usually adequately cleaned after 3 cleaning cycles. If a canister which has previously been used for sampling of ppm-level contaminants is to be used to sample low (ppb) concentrations of analytes, more rigorous cleaning will be required. Up to 100 cleaning cycles may be necessary. An effective and more efficient approach, however, is to put the contaminated canisters through 3 cleaning cycles, allow the canisters to sit for a couple of days, then repeat cleaning through three cycles, and check for cleanliness. Repeat this clean, store, and clean sequence as many times as necessary.

3.3.4 Canisters should be evacuated to a pressure of 6.7 Pa or less prior to sampling. It is recommended that cleaning and evacuation be conducted as near to the time of use as practical.

3.3.5 Canisters may be checked for leaks by pressurizing with clean nitrogen to 207 kPa, rechecking pressure after 24 hours. A pressure drop greater than 14 kPa indicates a leak.

3.4 Standard Preparation
3.4.1 Using nitrogen as the diluent gas, standards of the desired analytes plus internal standards are prepared in 6-liter Summa canisters using the Entech Model 4600 Dynamic Dilution System.

3.4.2 If electropolished Summa canisters are used, be sure to use humidified nitrogen as diluent gas, especially if polar
compounds are being analyzed. When using fused silica-coated canisters, the requirement for humidity is not critical, since contaminant molecules have lower affinity for the silica-coated surface than for bare stainless steel surfaces.

3.5 Sample Preparation

Prior to analysis, the pressure in each sample canister is increased to twice its original value, using zero-grade nitrogen as the diluent gas. After equilibration, this elevated pressure allows measured aliquots of the sample gas to be easily withdrawn for analysis.

3.6 Analysis

3.6.1 For samples expected to contain relatively high levels of contaminants (e.g., ppm levels), the Entech Model 7032L Loop Autosampler is used to withdraw approximately 1-mL aliquots of the sample air, diluted with nitrogen. This aliquot is cryofocused prior to introduction on to the GC/MS column.

3.6.2 For samples expected to contain levels of contaminants less than 1 ppm, the Entech Model 7032L Loop Autosampler, is used to withdraw 10- to 100-mL aliquots of the sample air, diluted with nitrogen. These aliquots are drawn into a sampling loop, then concentrated and cryofocused prior to introduction on to the GC/MS column.

3.6.3 Replicate analyses or subsequent aliquots of a different size may be drawn from a sample canister.

3.6.4 Mass spec conditions

<table>
<thead>
<tr>
<th>GC Column:</th>
<th>DB-1-MS, 30m x 0.320mm i.d.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial temperature:</td>
<td>35°C, hold for 5 minutes</td>
</tr>
<tr>
<td>Program rate:</td>
<td>10°C/minute</td>
</tr>
<tr>
<td>Final temperature:</td>
<td>280°C</td>
</tr>
</tbody>
</table>

zone temperatures:
- GC injector: 250°C
- Transfer line: 280°C
- Source: 230°C
- Analyzer: 150°C

<table>
<thead>
<tr>
<th>Electron energy:</th>
<th>70 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scan range:</td>
<td>24-250 AMU</td>
</tr>
</tbody>
</table>

4. Back-up Data

4.1 Detection Limits

Figure 4.1 shows chromatograms of 20-mL and 10-mL injections of a standard of approximately 5 ppb each of the four test compounds. Based on a 100-mL injected sample volume and a two-fold dilution, the estimated limits of detection are: \( n \)-hexane 0.2 ppb; tetrachloroethylene 0.4 ppb; toluene 1 ppb; and \( p \)-xylene 4 ppb. Detection limits were calculated based on peak heights which are three times the baseline noise.
4.2 Minimum Injection Volume

Table 4.2 shows the results of injections of a standard of approximately 50 ppb of each of the four test compounds, with injection volumes varying from 5 to 200 mL. Due to lack of acceptable reproducibility of the results from injections of 5 mL, it was concluded that 10 mL is the minimum injection volume which produces reliable results.

<table>
<thead>
<tr>
<th>mL</th>
<th>hexane</th>
<th>toluene</th>
<th>tetrachloro-ethylene</th>
<th>xylene</th>
<th>ISTD</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>135213</td>
<td>77835</td>
<td>244387</td>
<td>48399</td>
<td>1174510</td>
</tr>
<tr>
<td>5</td>
<td>299161</td>
<td>191667</td>
<td>426274</td>
<td>121338</td>
<td>1111884</td>
</tr>
<tr>
<td>10</td>
<td>4459700</td>
<td>4534540</td>
<td>6104070</td>
<td>4245197</td>
<td>1318405</td>
</tr>
<tr>
<td>10</td>
<td>3690372</td>
<td>3667848</td>
<td>5004722</td>
<td>3339190</td>
<td>1112885</td>
</tr>
<tr>
<td>20</td>
<td>12708131</td>
<td>14293658</td>
<td>18675442</td>
<td>13303503</td>
<td>789727</td>
</tr>
<tr>
<td>20</td>
<td>12661318</td>
<td>13970257</td>
<td>18132314</td>
<td>12841465</td>
<td>1073221</td>
</tr>
<tr>
<td>50</td>
<td>31717802</td>
<td>45084647</td>
<td>64610183</td>
<td>41904604</td>
<td>2195409</td>
</tr>
<tr>
<td>50</td>
<td>30678491</td>
<td>43439246</td>
<td>63863835</td>
<td>40392582</td>
<td>1716193</td>
</tr>
<tr>
<td>50</td>
<td>30201947</td>
<td>43346349</td>
<td>63159344</td>
<td>40179816</td>
<td>1569277</td>
</tr>
<tr>
<td>50</td>
<td>29278081</td>
<td>40377803</td>
<td>58893541</td>
<td>37513228</td>
<td>1636387</td>
</tr>
<tr>
<td>50</td>
<td>39971450</td>
<td>38043062</td>
<td>54059640</td>
<td>35324003</td>
<td>834744</td>
</tr>
<tr>
<td>100</td>
<td>61064562</td>
<td>126363870</td>
<td>244037259</td>
<td>122562739</td>
<td>2049239</td>
</tr>
<tr>
<td>100</td>
<td>56598966</td>
<td>111798212</td>
<td>213612977</td>
<td>109534835</td>
<td>2245114</td>
</tr>
<tr>
<td>150</td>
<td>161232524</td>
<td>221738723</td>
<td>451565957</td>
<td>267346044</td>
<td>1743758</td>
</tr>
<tr>
<td>150</td>
<td>160587701</td>
<td>213603130</td>
<td>438511070</td>
<td>249931430</td>
<td>1948079</td>
</tr>
<tr>
<td>200</td>
<td>109569656</td>
<td>30082355</td>
<td>618466534</td>
<td>346332656</td>
<td>2497457</td>
</tr>
<tr>
<td>200</td>
<td>211332078</td>
<td>310746877</td>
<td>617009392</td>
<td>322998984</td>
<td>2033987</td>
</tr>
</tbody>
</table>

4.3 Storage Stability

For storage stability studies, canisters were spiked with standards at approximately 25 ppb of each compound and stored at ambient temperatures. Two canisters were spiked with hexane and toluene, and two with tetrachloroethylene and xylene.
Aliquots were analyzed on day 0, and subsequently on days 3, 9, and 14. Table 4.3.1 shows the results, in percentages of theoretical amounts, for hexane and toluene. Similar data for tetrachloroethylene and xylene are shown in Table 4.3.2. These results are represented graphically for hexane in Figure 4.3.1.1, for toluene in Figure 4.3.1.2, for tetrachloroethylene in Figure 4.3.2.1, and for xylene in Figure 4.3.2.2.

### Table 4.3.1. Storage data for n-hexane and toluene at 25 ppb

<table>
<thead>
<tr>
<th>time (days)</th>
<th>n-hexane recovery (%)</th>
<th></th>
<th>toluene recovery (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>98.4</td>
<td>102.1</td>
<td>101.6</td>
<td>98.0</td>
</tr>
<tr>
<td>3</td>
<td>98.5</td>
<td>99.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>109.6</td>
<td>112.6</td>
<td>98.7</td>
<td>97.8</td>
</tr>
<tr>
<td>14</td>
<td>119.8</td>
<td>115.3</td>
<td>134.3</td>
<td>131.2</td>
</tr>
</tbody>
</table>

### Table 4.3.2. Storage data for tetrachloroethene and p-xylene at 25 ppb

<table>
<thead>
<tr>
<th>time (days)</th>
<th>tetrachloroethene recovery (%)</th>
<th></th>
<th>p-xylene recovery (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>98.9</td>
<td>104.9</td>
<td>100.8</td>
<td>95.4</td>
</tr>
<tr>
<td>3</td>
<td>101.8</td>
<td>105.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>81.9</td>
<td>80.0</td>
<td>87.3</td>
<td>94.0</td>
</tr>
<tr>
<td>14</td>
<td>93.4</td>
<td>87.5</td>
<td>89.9</td>
<td>88.1</td>
</tr>
</tbody>
</table>

![Figure 4.3.1.1](image1)

Storage test for 25 ppb of n-hexane

![Figure 4.3.1.2](image2)

Storage test for 25 ppb of toluene
A single canister was spiked with 100 ppm trichloroethane. This was analyzed immediately, and after storage up to 13 days. Results are tabulated in Table 4.3.3, and shown graphically in Figure 4.3.3.

Table 4.3.3 Storage test for 1,1,1-trichloroethane at 100 ppm

<table>
<thead>
<tr>
<th>time (days)</th>
<th>recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>102.0</td>
</tr>
<tr>
<td>3</td>
<td>100.4</td>
</tr>
<tr>
<td>5</td>
<td>107.2</td>
</tr>
<tr>
<td>7</td>
<td>96.8</td>
</tr>
<tr>
<td>12</td>
<td>91.4</td>
</tr>
<tr>
<td>13</td>
<td>91.3</td>
</tr>
<tr>
<td>17</td>
<td>98.3</td>
</tr>
</tbody>
</table>

4.4 Precision

The data in Section 4.4 were extracted from Table 4.2, and show the results of five replicate analyses of a canister spiked with 50 ppb of each of the 4 test compounds. Table 4.4.1 shows results for n-hexane along with statistical analysis. Table 4.4.2 shows similar results for toluene, Table 4.4.3 for tetrachloroethylene, and Table 4.4.4 for o-xylene.
<table>
<thead>
<tr>
<th>Table 4.4.1</th>
<th>Precision data for ( n )-hexane, 50-mL injection, 50 ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area Counts ( \times 10^7 )</td>
<td>\midrule</td>
</tr>
<tr>
<td>3.1718</td>
<td>\midrule</td>
</tr>
<tr>
<td>3.0627</td>
<td>mean = 3.2370</td>
</tr>
<tr>
<td>3.0202</td>
<td>SD = 0.4339</td>
</tr>
<tr>
<td>2.9278</td>
<td>CV = 13.40 %</td>
</tr>
<tr>
<td>3.9971</td>
<td>\midrule</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 4.4.2</th>
<th>Precision data for toluene, 50-mL injection, 50 ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area Counts ( \times 10^7 )</td>
<td>\midrule</td>
</tr>
<tr>
<td>4.5085</td>
<td>\midrule</td>
</tr>
<tr>
<td>4.3439</td>
<td>mean = 4.2058</td>
</tr>
<tr>
<td>4.3346</td>
<td>SD = 0.2814</td>
</tr>
<tr>
<td>4.0378</td>
<td>CV = 6.69 %</td>
</tr>
<tr>
<td>3.8043</td>
<td>\midrule</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 4.4.3</th>
<th>Precision data for tetrachloroethylene, 50-mL injection, 50 ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area Counts ( \times 10^7 )</td>
<td>\midrule</td>
</tr>
<tr>
<td>6.4610</td>
<td>\midrule</td>
</tr>
<tr>
<td>6.3864</td>
<td>mean = 6.0917</td>
</tr>
<tr>
<td>6.3159</td>
<td>SD = 0.4429</td>
</tr>
<tr>
<td>5.8894</td>
<td>CV = 7.27 %</td>
</tr>
<tr>
<td>5.4060</td>
<td>\midrule</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 4.4.4</th>
<th>Precision data for xylene, 50-mL injection, 50 ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area Counts ( \times 10^7 )</td>
<td>\midrule</td>
</tr>
<tr>
<td>4.1905</td>
<td>\midrule</td>
</tr>
<tr>
<td>4.0393</td>
<td>mean = 3.9603</td>
</tr>
<tr>
<td>4.0180</td>
<td>SD = 0.2690</td>
</tr>
<tr>
<td>3.7513</td>
<td>CV = 6.79 %</td>
</tr>
<tr>
<td>3.5324</td>
<td>\midrule</td>
</tr>
</tbody>
</table>

4.5 Canister cleaning.
4.5.1 Figure 4.5.1 shows a chromatogram after 3 cleaning cycles of a canister which had contained 33 ppm trichloroethane. A 1-mL aliquot was sampled by loop injection without pre-concentration. The canister is adequately clean for sampling and
analysis at the ppm level.

Figure 4.5.1 Total ion chromatogram of a MiniCan that had contained 33 ppm of 1,1,1-trichloroethane and then was cleaned 3 cycles. Analysis by loop injection. Arrow shows the retention time of 1,1,1-trichloroethane.

4.5.2 Figure 4.5.2 shows a chromatogram after 100 cleaning cycles of a canister which had contained 100 ppm of trichloroethane. A 100-mL aliquot was sampled for pre-concentration prior to injection. The canister is adequately clean for sampling and analysis at the ppb level. It is recommended that highly contaminated canisters be cleaned for 3 cycles, allowed to sit for several days, then cleaned for 3 more cycles and tested for cleanliness. Repeat this sequence until acceptable cleanliness is achieved.

Figure 4.5.2 Total ion chromatogram of a MiniCan that had previously contained 100 ppm of 1,1,1-Trichloroethane and had been cleaned 100 cycles. 1,1,1-trichloroethane elutes at 11.4 min.

REFERENCES


5. Formaldehyde and VOC’s in Indoor Air Quality Determinations by GC/MS, Entech Instruments Applications Note 101, Entech Instruments, Inc., Simi Valley, CA.


9. Certified laboratories which will analyze Entech Canisters on a fee-for-analysis basis include Galson Laboratories, East Syracuse, NY, and Aerotech Laboratories, Inc., Phoenix, AZ.
Ozone In Workplace Atmospheres
(Impregnated Glass Fiber Filter)

Related Information: Chemical Sampling - Ozone

<table>
<thead>
<tr>
<th>Method no.:</th>
<th>ID-214</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix:</td>
<td>Air</td>
</tr>
</tbody>
</table>

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)
TWA: 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
- **TWA**
  - Validated Range: 0.070 t 0.224 ppm
  - CV<sub>pooled</sub>: 0.045
  - Bias: +0.014
  - Overall Error: ±10.4%
- **STEL**
  - Validated Range: 0.330 ppm
  - CV<sub>pooled</sub>: 0.054
  - Bias: -0.015
  - Overall Error: ±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.
1. Introduction

This method describes the sample collection and analysis of airborne ozone (O₃). 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.

The January 2008 method revision consists of updated instructions for the preparation of IGFFs. The purpose of the updated instructions is to describe techniques to be used for the preparation of media with low residual nitrate levels and also for the reduction of nitrate formation during media storage. These instructions are presented in Section 2.1.3.

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 withtrans-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:

<table>
<thead>
<tr>
<th>Date</th>
<th>Method</th>
<th>Principle</th>
<th>Collection Medium</th>
<th>Major Advantages</th>
<th>Major Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1960s - present</td>
<td>Detector tubes</td>
<td>Oxidation of indigo by ozone resulting in white color</td>
<td>Direct-read</td>
<td>Simple, rapid</td>
<td>Interferences, more a spot check for exposure measurement</td>
</tr>
<tr>
<td>Before 1977</td>
<td>1% Neutral buffered KI</td>
<td>Reaction with KI</td>
<td>1% KI, phosphate buffer, pH=6.8</td>
<td>Simple, rapid, and sensitive</td>
<td>Bubbler, unstable, and interferences from all oxidants</td>
</tr>
<tr>
<td>1977 - 80</td>
<td>Alkaline KI</td>
<td>Reaction with KI</td>
<td>1% KI, 1.0 N NaOH, pH&gt;11</td>
<td>Simple, rapid, and sensitive</td>
<td>Bubbler, unstable, sampling rate dependence, and interferences from all oxidants</td>
</tr>
<tr>
<td>1983 - 92</td>
<td>Ozone meter (AID Model 560)</td>
<td>Chemiluminescence</td>
<td>Direct reading instrument</td>
<td>Very sensitive, direct-reading, very specific</td>
<td>No data logging and bulky instrument requiring ethylene (flammable gas) or Ethychem (ethylene in CO₂)</td>
</tr>
<tr>
<td>1986</td>
<td>Neutral buffered (KIBRT)</td>
<td>Reaction with KI and Na₂S₂O₃, Measurement of excess I₂</td>
<td>1% KI, a known amount of thiosulfate, 2% KBr</td>
<td>Simple, rapid sensitive, stable and some independence from sampling rate</td>
<td>Bubbler, interferences from all oxidants. Potential contamination.</td>
</tr>
<tr>
<td>1990 - 91 (Lab use only)</td>
<td>Glass beads trans-stilbene</td>
<td>Reaction with olefins</td>
<td>Glass beads coated with trans-stilbene</td>
<td>Simple, rapid, sensitive and O₃ specific</td>
<td>Recovery dependent on humidity</td>
</tr>
<tr>
<td>1990 - 91 (Lab use only)</td>
<td>trans-stilbene and mesitol</td>
<td>Reaction with olefins</td>
<td>0.05% trans-stilbene + 0.5% mesitol in a mixture of acetonitrile/water (9:1)</td>
<td>Simple, rapid, sensitive and O₃ specific</td>
<td>Flammable liquid, bubbler used for sample collection</td>
</tr>
<tr>
<td>1992 - present</td>
<td>Ozone meter (AED-030)</td>
<td>Semi-conductor sensor</td>
<td>Direct reading instrument</td>
<td>Simple, rapid, sensitive and easy to use</td>
<td>No data logging capacity, instrument treads to drift</td>
</tr>
<tr>
<td>This method</td>
<td>IGFF</td>
<td>Reaction with nitrite</td>
<td>Nitrite-coated IGFFs</td>
<td>Simple, rapid, sensitive</td>
<td>Interference from SO₂</td>
</tr>
</tbody>
</table>

1.2 Principle

Ozone is collected using two nitrite-impregnated glass fiber filters (IGFFs). The second IGFF serves as a backup filter. The collected O₃ converts nitrite (NO₂⁻) to nitrate (NO₃⁻) via oxidation as shown by the following chemical reaction:

\[ \text{NO}_2^- + \text{O}_3 \rightarrow \text{NO}_3^- + \text{O}_2 \]

The resultant NO₃⁻ 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 O₃ collected from the amount of NO₃⁻ 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 O₃ exposure. The method is also capable of monitoring Food and Drug Administration limit of 0.05 ppm O₃ in enclosed
spaces (21 CFR 801.415). The U.S. Environmental Protection Agency (EPA) has established a National Ambient Air Quality Standard (NAAQS) for O₃ 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 O₃ exposure.

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

1.3.3 The method is "relatively" specific for O₃ (as NO₃⁻) in the presence of other nitrogen-containing substances, such as nitrogen dioxide (NO₂).

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 (SO₂) 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 SO₂ and allow O₃ 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 NO₃⁻) when using a 5-mL solution volume. This corresponds to 0.008 ppm O₃ for a 90-L air volume.

1.4.3 The quantitative detection limit was 1.25 µg/mL or 6.25 µg (as NO₃⁻) when using a 5-mL solution volume. This corresponds to 0.03 ppm O₃ 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 NO₃⁻). The sensitivity was 3.7 × 10⁵ area units per 1 µg/mL. A Dionex Series 4500i ion chromatograph with a LinearUVIS-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:

<table>
<thead>
<tr>
<th></th>
<th>TWA</th>
<th>STEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV</td>
<td>0.045</td>
<td>0.054</td>
</tr>
<tr>
<td>Bias</td>
<td>+0.014</td>
<td>-0.015</td>
</tr>
<tr>
<td>OE</td>
<td>±10.4%</td>
<td>±12.3%</td>
</tr>
</tbody>
</table>

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 O₃ 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 O₃. 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 O₃, and the average breakthrough was 7.5% at a concentration of 0.4 ppm O₃. However, no breakthrough was found at a concentration of 0.6 ppm O₃ 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 O₃ 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$_3$ 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$_3$ will also interfere (negative). If interference from SO$_2$ is expected, an oxidizer pretube, such as the tube commonly used for converting NO to NO$_2$ (OSHA Method ID-182 or ID-190), can be used to effectively remove SO$_2$ and allow O$_3$ 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$_3^-$ 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$_3^-$ 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 a 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.

<table>
<thead>
<tr>
<th>CAS No.</th>
<th>10028-15-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>O$_3$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>47.997</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.6 (liquid) @ -183°C</td>
</tr>
<tr>
<td>Melting point</td>
<td>-192°C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>-112°C</td>
</tr>
<tr>
<td>Vapor density (air = 1)</td>
<td>1.65</td>
</tr>
<tr>
<td>Synonym</td>
<td>Triatomic oxygen</td>
</tr>
<tr>
<td>Appearance and odor</td>
<td>Colorless at concentrations noted in industry. Pungent characteristic odor usually associated with electric sparks.</td>
</tr>
</tbody>
</table>

1.8 Toxicology (Ref. 5.13)

Information listed within this section is a synopsis of current knowledge of the physiological effects of O$_3$ 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\textsubscript{2}, gas interfere in the analysis of NO\textsubscript{3} if collected on the same IGFFs. However, if interference from SO\textsubscript{2} is expected, a pretube, such as the tube used for converting NO to NO\textsubscript{2}, can be used to effectively remove SO\textsubscript{2}, and allow O\textsubscript{3} to pass through to the IGFFs. If the amount of SO\textsubscript{2} 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\textsubscript{2} is present prior to O\textsubscript{3} 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 prepared following the instructions below:

Apparatus
a. Glass fiber filters (GFFs), 37-mm (Gelman Sciences, Ann Arbor, MI, Type A/E, product number 61652)
b. Glass beakers, 400-500-mL and 10-20mL
c. 100-mL volumetric flask
d. Eppendorf pipet capable of dispensing 0.4 mL or glass pipet capable of dispensing 0.4 mL
e. Oven capable of heating to 100 °C (to dry the impregnated filters there must be a nitrogen atmosphere in the oven, or use a desiccator with a nitrogen atmosphere)
f. Forceps
g. Cassette gel sealing bands
h. Two-section polystyrene cassettes, 37-mm diameter with end plugs (Millipore Corp. Bedford MA, part number MAWP037 AO)
i. Chemicals (Reagent grade or better)

Sodium nitrite (NaNO\textsubscript{2}), 99.99%
Potassium carbonate (KCO\textsubscript{3}), 99%
Glycerol, 99.5%

Note: Before coating, the glass fiber filter must be thoroughly cleaned with deionized water to remove any trace amounts of soluble nitrate compounds. Filter impregnation requires the use of very pure chemicals, and careful handling of both chemicals and IGFFs to avoid contamination from ambient ozone in the air and soluble nitrate containing chemicals. The sodium nitrite, IGFFs, and loaded cassettes should be protected from ambient ozone in aluminized bags.

Procedure

a. Clean each GFF one at a time using three 400 or 500-mL beakers filled with deionized water. Take the GFF out of the box with cleaned forceps. Swish it back and forth in the first beaker, then in the second beaker, and finally in the third beaker. Place it on a clean, nitrate-free surface to support the outside edge of the GFF (we used the lips of 20-mL beakers). Place the filters
into an oven to dry for 30 min at 100 °C. Remove the filters from the oven when they are dry and allow them to cool to room temperature for 15-30 min.

b. Prepare the impregnating solution just prior to use. The impregnating solution, in the volumetric flask, will become contaminated from the air slowly, such that the nitrate levels become too high after 4 hours. To make the solution place 0.3 g NaNO2, 0.28 g KCO3, and 1 mL of glycerol in a 100 mL volumetric flask and dilute to the mark with deionized water. Shake the flask well to mix the contents.

c. Place each cleaned filter on a 10 or 20-mL beaker.

d. Slowly add 0.4 mL of the impregnating solution, making sure the entire filter is saturated with the solution.

e. Carefully place each beaker (with impregnated filter on top) into a drying oven with a nitrogen atmosphere, at 100 °C, for 30 min. If a drying oven with nitrogen atmosphere is not available, dry the filters for 1-2 hours in a desiccator under nitrogen. Ambient air contains ozone, so the filters must be protected from contamination by used of a nitrogen atmosphere.

f. Cool the filters a few minutes. Using forceps remove the IGFFs from the beakers and load the cassettes with two filters, one on top of the other both with the rough side up (grid side down).

g. Firmly close the cassette, make sure the end plugs are in place, and seal it with a gel band. Once the gel band is dry, place the cassette into an aluminized bag for storage until used in the workplace. Instruct the industrial hygienist to return the cassette to the analytical laboratory using the aluminized bag for transport. Any IGFFs not used to load cassettes should be immediately placed into aluminized bags for storage.

h. IGFFs stored in this fashion are stable for at least 45 days.

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 SO2 in the sampled air.

If there is reason to suspect the sampled air could contain SO2, an oxidizer tube must be used to remove the SO2. 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 O3 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 O3 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 O3 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\textsubscript{2} 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.](image)

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-µm 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 (Na₂CO₃), 99%
- Sodium bicarbonate (NaHCO₃), 99%
- Sodium nitrate (NaNO₃), 99.9%
- Deionized water (DI H₂O)

3.3.2 Eluent (1.0 mM Na₂CO₃ + 1.0 mM NaHCO₃):
Dissolve 0.424 g Na₂CO₃ and 0.336 g NaHCO₃ in 4.0 L DI H₂O. Sonicate this solution and degas under vacuum for 15 min.

Nitrate (NO₃⁻) stock standard (1,000 µg/mL):
Dissolve and dilute 1.3710 g of NaN0₃ to 1.0 L with DI H₂O. 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 (O₃) under controlled conditions, or media can be spiked with the analyte (NO₃⁻). 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 (NO₃⁻) standard solutions, 100, 10, and 1 µg/mL: Pipette appropriate volumes of the 1,000 µg/mL as NO₃⁻ 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 NO₃⁻ working standards in eluent. A suggested scheme for preparing a series of working standards using 10-mL final solution volumes is shown below:
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).

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

Sample Preparation

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

Pipette 5.0 mL of DI H₂O 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 NO₃⁻) within the range of the standards specified.

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

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

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 IGF (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 NO₃⁻ 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.

Comparison of a Standard and a Sample
This figure shows a sample chromatogram superimposed over a standard chromatogram. The sample chromatogram shows the chromatographic separation of the nitrite peak from the nitrate peak in a sample. The retention times for the nitrate peak in the sample and the nitrate peak in the standard are almost identical and show that the separation of nitrite and nitrate is adequate.

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 NaCO₃/1.0 mM NaHCO₃
- **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 uL

**Pump**

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

**Chromatogram**

- **Run time:** 5 min
- **Peak retention time:** ~3.00 min for NO₃⁻

* 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:
This figure shows a sample chromatogram superimposed over a blank sample chromatogram. The sample chromatogram represents nitrate from an ozone concentration of approximately two times the PEL for a 180 min sample. The nitrate normally occurring in a blank sample is shown for illustrative purposes. Detector response and column retention times were obtained using equipment and analytical conditions specified in this method.

* 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 $\mu$g/mL.

3.7.3 Determine total $\mu$g for each sample and blank. Perform a blank correction for each IGFF. Subtract the total $\mu$g blank value from each total $\mu$g sample value.

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

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

$$A = A_s - A_b$$

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

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

where:

- $A_b$ = Total $\mu$g $\text{O}_3$ in blank
- $A_s$ = Total $\mu$g $\text{O}_3$ in sample
- $A$ = $\mu$g $\text{O}_3$ after blank correction
- $(\mu\text{g/mL }\text{NO}_3^-)_b$ = Amount found
\[
(\mu g/mL \text{NO}_3^-)_s = \text{Amount found (from calibration curve) in sample}
\]
\[
(SoI\text{Vol})_b = \text{Blank solution volume (mL) from Section 3.5.2 (normally 5 mL)}
\]
\[
(SoI\text{Vol})_s = \text{Sample solution volume (mL) from Section 3.5.2 (normally 5 mL)}
\]
\[
CF = \text{Conversion factor} = \frac{\text{O}_3}{\text{NO}_3^-} = 0.7742
\]
\[
\text{Mol Vol} = \text{Molar volume (L/mol)} = 24.45 (25°C and 760 mmHg)
\]
\[
\text{AV} = \text{Air volume (L)}
\]
\[
\text{Mol Wt} = \text{Molecular weight for O}_3 = 47.997 \text{ (g/mol)}
\]

3.8 Add the results of the first and second filters to give one final O$_3$ 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$_3$.

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$_3$. 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$_3$ 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. Interface 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:

\[ \text{OE} \% = \pm (|\text{bias}| + 2\text{CV}) \times 100\% \text{ (at the 95\% confidence level)} \]

Where / is the respective sample pool being examined.

**Block Diagram of the Laboratory Generation System**

![Block Diagram of the Laboratory Generation System](image)

Text Version: Lab air passes through an Air Purifier and then enters the Flow-Temp-Humidity Control System. Lab Water passes through an Ionic Exchange Column, where it is purified, and then enters the Flow-Temp-Humidity Control System. The Flow-Temp-Humidity Control System generates properly conditioned dilution air that enters the Mixing Chamber. Ozone is produced by the Ozone Generator System and it enters the Mixing Chamber to be completely mixed with dilution air to produce the ozone test atmosphere. The ozone test atmosphere enters the Active Sampling Manifold. The Active Sampling Manifold provides a means to sample the ozone atmosphere such as described in OSHA Method ID 214.
The ozone test atmosphere next enters an Ozone Passive Exposure Chamber where diffusive samplers can be exposed to the ozone test atmosphere. The ozone test atmosphere next passes through a Dry Test Meter where the total air/ozone volume is measured. Finally, the ozone test atmosphere enters the laboratory Exhaust system and goes to waste.

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$_3$ (as NaNO$_3$) 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 µg NO$_3^-$. 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$_3$ collection using IGFFs.

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone (as NO$_3$^-) Analysis - Desorption Efficiency (DE)</td>
</tr>
<tr>
<td>level (×)</td>
</tr>
<tr>
<td>0.5 × PEL</td>
</tr>
<tr>
<td>1 × PEL</td>
</tr>
<tr>
<td>2 × PEL</td>
</tr>
<tr>
<td>all levels</td>
</tr>
</tbody>
</table>

*CV$_1$ (pooled)

4.2 Sampling and Analysis

To determine the precision and accuracy of the method, known concentrations of O$_3$ were generated, samples were collected, and analyzed.

4.2.1 Procedure:

1. Test atmospheres of O$_3$ were generated using two ozone generators (Model 565, ThermoElectron Instruments, Hopkinton, MA) simultaneously to achieve as high O$_3$ concentrations as possible. The O$_3$ 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 oxygen 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$_3$ 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$_3$ 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 CVT for the TWA sampling and analytical method.
Table 2a  
Ozone sampling and Analysis - TWA PEL Determinations  

<table>
<thead>
<tr>
<th>level (°)</th>
<th>N</th>
<th>ave recovery</th>
<th>SD</th>
<th>CV₂</th>
<th>OE₂ (±%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>8</td>
<td>1.032</td>
<td>0.060</td>
<td>0.059</td>
<td>14.9</td>
</tr>
<tr>
<td>1</td>
<td>7</td>
<td>1.071</td>
<td>0.023</td>
<td>0.022</td>
<td>11.5</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>0.937</td>
<td>0.028</td>
<td>0.030</td>
<td>12.3</td>
</tr>
<tr>
<td>all levels</td>
<td>22</td>
<td>1.014</td>
<td>-</td>
<td>0.041*</td>
<td>9.7 **</td>
</tr>
</tbody>
</table>

* CV₂ (pooled) - ** OE₂ (pooled)

The total pooled coefficients of variation (CVₜ), bias, and total overall error (OEₜ) are as follows:

CVₜ (pooled) = 0.045  
bias = + 0.014  
OEₜ = 10.4%  

(Note: The CVₜ and OEₜ 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 O₃ Concentration = 0.33 ppm)

<table>
<thead>
<tr>
<th>level(°)</th>
<th>N</th>
<th>mean ppm found</th>
<th>SD</th>
<th>CV</th>
<th>recovery</th>
<th>OE</th>
</tr>
</thead>
<tbody>
<tr>
<td>STEL</td>
<td>5</td>
<td>0.325</td>
<td>0.018</td>
<td>0.054</td>
<td>98.5%</td>
<td>±12.3%</td>
</tr>
</tbody>
</table>

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 O₃ gas collected on the first and second IGFFs were determined. The collection efficiency (CE) was calculated by dividing the amount of O₃ collected in the first filter by the total amount of O₃ collected in the first and second IGFFs.

Results: The results in Table 3 show a CE of 100%. No O₃ was found in the second IGFF for the CE experiment and indicates the IGFFs have adequate collection of O₃ near the PEL.

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

| ppm O₃ |
|---------|---------|-------|
| sample no. | 1ˢᵗ IGFF | 2ⁿᵈ IGFF | CE, % |
| 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 O₃)

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× 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 O₃ generators and the generation system, larger O₃ 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 O₃ collected in the first and second IGFFs.

**Results:** For measurements near the TWA PEL, no breakthrough of O₃ into the second section was found at an approximate concentration of 0.2 ppm O₃ (Table 4a), and indicates the first IGFF has adequate retention of O₃ at 2 times TWA PEL. However, the average breakthrough was 7.5% at an approximate concentration of 0.4 ppm O₃ ([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 O₃ ([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 O₃ ([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

<table>
<thead>
<tr>
<th>ppm O₃</th>
<th>1st IGFF</th>
<th>2nd IGFF</th>
<th>Breakthrough, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample no.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.242</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.281</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0.190</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0.227</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0.238</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>0.215</td>
<td>ND</td>
<td>0</td>
</tr>
</tbody>
</table>

**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 O₃)

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

<table>
<thead>
<tr>
<th>ppm O₃</th>
<th>1st IGFF</th>
<th>2nd IGFF</th>
<th>CE, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample no.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.425</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.385</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0.395</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0.363</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0.383</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>0.342</td>
<td>ND</td>
<td>0</td>
</tr>
</tbody>
</table>
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.  
(c) Statistical analysis - N = 8; mean = 7.5; SD = 1.5; CV = 0.20

<table>
<thead>
<tr>
<th>sample no.</th>
<th>1st IGFF</th>
<th>2nd IGFF</th>
<th>Breakthrough, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.563</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.600</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0.586</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0.661</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0.566</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>0.558</td>
<td>ND</td>
<td>0</td>
</tr>
</tbody>
</table>

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$_3$)

<table>
<thead>
<tr>
<th>sample no.</th>
<th>1st IGFF</th>
<th>2nd IGFF</th>
<th>Breakthrough, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.440</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.308</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0.333</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0.346</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0.306</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>0.334</td>
<td>ND</td>
<td>0</td>
</tr>
</tbody>
</table>

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$_3$)

4.5 Storage Stability

Procedure: A study was conducted to assess the stability of the NO$_2^-$ + O$_3$ reaction product, NO$_3^-$ 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>
<thead>
<tr>
<th>Day</th>
<th>N</th>
<th>Mean O₃ Found</th>
<th>SD</th>
<th>CV</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7</td>
<td>0.122</td>
<td>0.005</td>
<td>0.038</td>
<td>99.2</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>0.120</td>
<td>0.004</td>
<td>0.036</td>
<td>97.6</td>
</tr>
<tr>
<td>15</td>
<td>6</td>
<td>0.135</td>
<td>0.002</td>
<td>0.015</td>
<td>109.8</td>
</tr>
<tr>
<td>30</td>
<td>6</td>
<td>0.116</td>
<td>0.006</td>
<td>0.052</td>
<td>94.3</td>
</tr>
</tbody>
</table>

**Storage Stability**

![Storage Stability Graph](image)

**Figure 3**

Text Version: Figure 3 is a graph of the storage stability data shown in Table 5. The graph shows percent ozone recovery plotted on the y-axis against days of storage time plotted on the x-axis. The storage stability is excellent, with approximately 94% of the ozone recovered after 30 days of ambient storage.

**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>
<thead>
<tr>
<th>Day</th>
<th>N</th>
<th>Mean O₃ Found</th>
<th>SD</th>
<th>CV</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 6**

Humidity Test - Ozone
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 NaNO₃ (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 NO₃⁻ at the 99.8% confidence level. The quantitative detection limit is 1.25 µg/mL as NO₃⁻.

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 O₃.

<table>
<thead>
<tr>
<th>Level</th>
<th>RH, %</th>
<th>N</th>
<th>Mean O₃ Found</th>
<th>SD</th>
<th>CV</th>
<th>Taken</th>
<th>Recovery, %</th>
<th>Fcrit</th>
<th>Fcalc</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 × PEL</td>
<td>30</td>
<td>7</td>
<td>0.073</td>
<td>0.008</td>
<td>0.107</td>
<td>0.070</td>
<td>104</td>
<td>5.93</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>8</td>
<td>0.072</td>
<td>0.004</td>
<td>0.059</td>
<td>0.070</td>
<td>103</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>7</td>
<td>0.060</td>
<td>0.001</td>
<td>0.024</td>
<td>0.058</td>
<td>103</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 × PEL</td>
<td>30</td>
<td>6</td>
<td>0.119</td>
<td>0.007</td>
<td>0.059</td>
<td>0.115</td>
<td>103</td>
<td>6.11</td>
<td>2.62</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>7</td>
<td>0.118</td>
<td>0.003</td>
<td>0.022</td>
<td>0.110</td>
<td>107</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>7</td>
<td>0.101</td>
<td>0.002</td>
<td>0.022</td>
<td>0.098</td>
<td>103</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 × PEL</td>
<td>30</td>
<td>7</td>
<td>0.174</td>
<td>0.005</td>
<td>0.030</td>
<td>0.172</td>
<td>101</td>
<td>6.01</td>
<td>2.71</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>7</td>
<td>0.222</td>
<td>0.006</td>
<td>0.028</td>
<td>0.224</td>
<td>99.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>7</td>
<td>0.231</td>
<td>0.006</td>
<td>0.027</td>
<td>0.237</td>
<td>97.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>O₃ (as NO₃⁻) Level</th>
<th>Blank PA</th>
<th>0.1 µg/mL PA</th>
<th>0.2 µg/mL PA</th>
<th>0.5 µg/mL PA</th>
<th>1.0 µg/mL PA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample No. 1</td>
<td>2.05</td>
<td>2.73</td>
<td>2.25</td>
<td>3.17</td>
<td>5.87</td>
</tr>
<tr>
<td>Sample No. 2</td>
<td>1.98</td>
<td>2.60</td>
<td>3.15</td>
<td>4.15</td>
<td>4.99</td>
</tr>
<tr>
<td>Sample No. 3</td>
<td>2.02</td>
<td>1.81*</td>
<td>3.15</td>
<td>3.21</td>
<td>4.98</td>
</tr>
<tr>
<td>Sample No. 4</td>
<td>2.03</td>
<td>2.60</td>
<td>3.23</td>
<td>4.09</td>
<td>5.76</td>
</tr>
<tr>
<td>Sample No. 5</td>
<td>2.02</td>
<td>2.68</td>
<td>4.55*</td>
<td>4.12</td>
<td>5.81</td>
</tr>
<tr>
<td>Sample No. 6</td>
<td>1.74*</td>
<td>2.69</td>
<td>3.79</td>
<td>3.24</td>
<td>5.81</td>
</tr>
</tbody>
</table>

* Outlier
PA - Integrated Peak Area (NO₃⁻)/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 (\(\hat{Y}_0\)) at each X.

Using the equations:

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

\[
Q_1 = \frac{3S_y}{m}
\]

\[
Q_2 = (3.33)Q_1
\]

**Text Version**: First subtract each obtained response from its predicted response, and then square that difference. Sum all these values. Divide the sum by the number of data points minus two. Take the square root of that value. The result is the standard error of the regression line.
Therefore, 
\[ Q_1 = (3S_y/m = 0.37 \, \mu g/mL \text{ as NO}_3^- \]
\[ \Rightarrow \quad 1.85 \, \mu g \text{ as NO}_3^- \text{ (5-mL sample volume)} \]
\[ \Rightarrow \quad 0.008 \, \text{ppm O}_3 \text{ (90-L air volume)} \]
\[ Q_2 = (3.33)Q_1 \]
\[ \Rightarrow \quad 0.027 \, \text{ppm O}_3 \text{ (90-L air volume)} \]

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
- \( Q_1 \) = qualitative detection limit
- \( Q_2 \) = 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\(^3\)/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>
<thead>
<tr>
<th>Set #</th>
<th>Method</th>
<th>( \text{O}_3 ) Found, ppm</th>
<th>N</th>
<th>SD</th>
<th>CV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AKI</td>
<td>0.070</td>
<td>3</td>
<td>0.006</td>
<td>0.086</td>
</tr>
<tr>
<td></td>
<td>IGFF</td>
<td>0.072</td>
<td>8</td>
<td>0.004</td>
<td>0.056</td>
</tr>
<tr>
<td></td>
<td>OPS</td>
<td>0.073</td>
<td>4</td>
<td>0.003</td>
<td>0.041</td>
</tr>
<tr>
<td>2</td>
<td>AKI</td>
<td>0.110</td>
<td>3</td>
<td>0.002</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>IGFF</td>
<td>0.118</td>
<td>7</td>
<td>0.003</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td>OPS</td>
<td>0.129</td>
<td>7</td>
<td>0.017</td>
<td>0.132</td>
</tr>
<tr>
<td>3</td>
<td>AKI</td>
<td>0.224</td>
<td>3</td>
<td>0.008</td>
<td>0.036</td>
</tr>
<tr>
<td></td>
<td>IGFF</td>
<td>0.210</td>
<td>7</td>
<td>0.006</td>
<td>0.029</td>
</tr>
<tr>
<td></td>
<td>OPS</td>
<td>0.187</td>
<td>7</td>
<td>0.012</td>
<td>0.064</td>
</tr>
</tbody>
</table>

Table 8
Comparison of Methods (Summary)
(25°C and 50% RH)
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 \(O_3\)) 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 \(SO_2\) as the active sampler (Section 4.9). In a recent paper (Ref. 5.10), the authors indicated that \(SO_2\) should not interfere with the passive sampler collection of \(O_3\); 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 \(O_3\) in previous methods (Refs. 5.1–5.2, 5.4). Several tests were conducted to evaluate any possible interference from \(NO_2\) or \(SO_2\).

**Procedure:** Possible interferences from \(NO_2\) and \(SO_2\) were tested using several sets of IGFF/cassette samples. A test was conducted by taking four samples at approximately 6 ppm \(NO_2\) and compared to four samples without \(NO_2\) which served as "control" samples. Several tests were conducted to evaluate any \(SO_2\) interference by comparing results of six samples with \(SO_2\) to another four to six samples without \(SO_2\) present. These tests included two different \(SO_2\) concentrations and use of oxidizer tubes for removal of \(SO_2\) from the sampled air prior to \(O_3\) 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\(_2\)) during sampling for NO. The two types of oxidizer tubes are:

<table>
<thead>
<tr>
<th>Tube Label</th>
<th>Substrate</th>
<th>Abbrev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidizer Special</td>
<td>Chromate impregnated sand</td>
<td>OS</td>
</tr>
<tr>
<td>Misc-Spec</td>
<td>Chromate impregnated material</td>
<td>MS</td>
</tr>
<tr>
<td></td>
<td>(Composition of substrate unknown)</td>
<td></td>
</tr>
</tbody>
</table>

Both tube labels are designations given by SKC. Chromate impregnated sorbent has been shown to effectively remove \(SO_2\) 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:

<table>
<thead>
<tr>
<th>Sample Set No.</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
<td>(O_3) with and without (NO_2)</td>
</tr>
<tr>
<td>2)</td>
<td>(O_3) with and without (SO_2) (3.41 ppm)</td>
</tr>
<tr>
<td>3)</td>
<td>(O_3) with and without (SO_2) (1.06 ppm)</td>
</tr>
<tr>
<td>4)</td>
<td>(O_3) with and without (SO_2) (0.35 ppm)</td>
</tr>
<tr>
<td>5)</td>
<td>(O_3) + (SO_2) with and without OS oxidizer</td>
</tr>
<tr>
<td>6)</td>
<td>(O_3) + (SO_2) with OS oxidizer before and after conditioning</td>
</tr>
<tr>
<td>7)</td>
<td>(O_3) + (SO_2) with and without MS oxidizer</td>
</tr>
<tr>
<td>8)</td>
<td>(O_3) + (SO_2) with MS oxidizer before and after conditioning</td>
</tr>
</tbody>
</table>
Comparison study between 50% and 80% RH for O$_3$ + SO$_2$ 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)

<table>
<thead>
<tr>
<th>Sample Set #</th>
<th>Interferant Conc, ppm</th>
<th>Oxidizer (Yes or No)</th>
<th>Conditioning (Yes or No)</th>
<th>N</th>
<th>Mean O$_3$, ppm</th>
<th>SD O$_3$, ppm</th>
<th>CV%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NO$_2$, 6.38</td>
<td>No</td>
<td>NA</td>
<td>4</td>
<td>0.129</td>
<td>0.007</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>NO$_2$, 0</td>
<td>NA</td>
<td>NA</td>
<td>4</td>
<td>0.134</td>
<td>0.003</td>
<td>20.</td>
</tr>
<tr>
<td>2</td>
<td>SO$_2$, 3.41</td>
<td>No</td>
<td>NA</td>
<td>6</td>
<td>0.168</td>
<td>0.009</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>SO$_2$, 0</td>
<td>NA</td>
<td>NA</td>
<td>6</td>
<td>0.169</td>
<td>0.013</td>
<td>7.8</td>
</tr>
<tr>
<td>3</td>
<td>SO$_2$, 1.06</td>
<td>No</td>
<td>NA</td>
<td>6</td>
<td>0.169</td>
<td>0.013</td>
<td>7.8</td>
</tr>
<tr>
<td>4</td>
<td>SO$_2$, 0.35</td>
<td>No</td>
<td>NA</td>
<td>6</td>
<td>0.169</td>
<td>0.013</td>
<td>7.8</td>
</tr>
<tr>
<td>5</td>
<td>SO$_2$, 1.06</td>
<td>Yes</td>
<td>Yes</td>
<td>6</td>
<td>0.141</td>
<td>0.009</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>SO$_2$, 0</td>
<td>NA</td>
<td>NA</td>
<td>6</td>
<td>0.142</td>
<td>0.009</td>
<td>6.0</td>
</tr>
<tr>
<td>6</td>
<td>SO$_2$, 1.06</td>
<td>Yes</td>
<td>No</td>
<td>6</td>
<td>0.108</td>
<td>0.012</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>SO$_2$, 1.06</td>
<td>Yes</td>
<td>No</td>
<td>6</td>
<td>0.141</td>
<td>0.009</td>
<td>6.3</td>
</tr>
<tr>
<td>7</td>
<td>SO$_2$, 1.06</td>
<td>Yes</td>
<td>Yes</td>
<td>6</td>
<td>0.153</td>
<td>0.005</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>SO$_2$, 0</td>
<td>NA</td>
<td>NA</td>
<td>4</td>
<td>0.154</td>
<td>0.001</td>
<td>0.9</td>
</tr>
<tr>
<td>8</td>
<td>SO$_2$, 1.06</td>
<td>Yes</td>
<td>No</td>
<td>6</td>
<td>0.141</td>
<td>0.014</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>SO$_2$, 1.06</td>
<td>Yes</td>
<td>No</td>
<td>6</td>
<td>0.153</td>
<td>0.005</td>
<td>3.1</td>
</tr>
<tr>
<td>9</td>
<td>SO$_2$, 1.06</td>
<td>Yes</td>
<td>Yes</td>
<td>6</td>
<td>0.153</td>
<td>0.005</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>SO$_2$, 1.06 *</td>
<td>Yes</td>
<td>Yes</td>
<td>5</td>
<td>0.145</td>
<td>0.008</td>
<td>5.8</td>
</tr>
</tbody>
</table>

* 80% RH was used instead of 50%

Notes:
(a) NA = Not applicable
(b) ND = None detectable (< 0.008 ppm O$_3$
(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$_3$

As shown in Sample Set #1, 6.38 ppm NO$_2$ caused no interference when sampling at 1.5 times TWA PEL ozone. When SO$_2$ 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$_3$ 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$_3$ recovery when SO$_2$ is present at 50% and 80% RH.

An additional test was conducted to determine if the passive monitor would be adversely affected by SO$_2$ in a similar fashion as the active sampler. Side-by-side active and passive samples were taken while varying the amount of SO$_2$. 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$_2$ interference as the active sampler. Detection limits are similar to what is stated earlier for both active and passive samplers.
<table>
<thead>
<tr>
<th>Sample Set #</th>
<th>Active or Passive</th>
<th>Interferant, SO₂ Concn (ppm)</th>
<th>N #</th>
<th>Mean O₃ ppm</th>
<th>SD O₃ ppm</th>
<th>CV %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Active</td>
<td>0</td>
<td>4</td>
<td>0.164</td>
<td>0.006</td>
<td>3.5</td>
</tr>
<tr>
<td>1</td>
<td>Active</td>
<td>1.89</td>
<td>3</td>
<td>ND</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>Passive</td>
<td>0</td>
<td>6</td>
<td>0.167</td>
<td>0.017</td>
<td>10.1</td>
</tr>
<tr>
<td>1</td>
<td>Passive</td>
<td>1.89</td>
<td>6</td>
<td>ND</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Active</td>
<td>0</td>
<td>2</td>
<td>0.132</td>
<td>0.007</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>Active</td>
<td>1.89</td>
<td>3</td>
<td>ND</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Passive</td>
<td>0</td>
<td>6</td>
<td>0.130</td>
<td>0.012</td>
<td>9.0</td>
</tr>
<tr>
<td>2</td>
<td>Passive</td>
<td>1.89</td>
<td>6</td>
<td>ND</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

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 H₂O 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 O₃ vapor (0.15 ppm O₃) after 58 days of storage.

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

After 28 days, the mean peak area was only a 2% increase over the value of Day 6.

After 57 days, the mean peak area was a 23% increase over the value of Day 0.

After blank correction and 58-day storage, the mean recovery of the O$_3$ collected was 95.5%. Mean O$_3$ found was 0.143 ppm after blank IGFF correction, and 4.0% CV.

### Table 11

<table>
<thead>
<tr>
<th>Sample Set #</th>
<th>Day i</th>
<th>N #</th>
<th>Mean * x10$^5$</th>
<th>SD x10$^5$</th>
<th>CV %</th>
<th>Ratio $X_i/X_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>5</td>
<td>2.02</td>
<td>0.025</td>
<td>1.3</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>6</td>
<td>2.20</td>
<td>0.080</td>
<td>3.7</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>4</td>
<td>2.93</td>
<td>0.100</td>
<td>3.5</td>
<td>1.45</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>6</td>
<td>2.33</td>
<td>0.200</td>
<td>8.6</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>4</td>
<td>2.37</td>
<td>0.091</td>
<td>3.8</td>
<td>1.02</td>
</tr>
<tr>
<td>3**</td>
<td>0</td>
<td>6</td>
<td>4.71</td>
<td>0.740</td>
<td>15.7</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>57</td>
<td>5</td>
<td>5.30</td>
<td>1.180</td>
<td>22.2</td>
<td>1.23</td>
</tr>
</tbody>
</table>

* Peak area.

** Ratio of IGFFs (mean peak area of Day 1 compared to that of mean Day 0).

** IGFFs were placed and stored in cassettes, scaled 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$_3$ 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$_3$ 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$_3^-$) 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$_2$/O$_3$ interference which diminishes the O$_3$ 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$_2$/O$_3$ atmosphere, a corresponding loss of O$_3$ was not noted. The ability of glass fiber filters to capture and convert SO$_2$, 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$_2$ in ambient air and on surfaces is complex. Fortunately, an oxidizer tube appears to completely remove SO$_2$ from the sampled stream. Presumably the SO$_2$ 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$_2$/O$_3$ atmosphere. For samples taken in the SO$_2$/O$_3$ atmosphere without oxidizer tubes, a significant increase in sulfate content was noted from the resultant oxidation of SO$_2$. The SO$_2$ 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 O3 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


5.5 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.


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 O₃ 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 cm² or 0.021 ft²), 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 cm³/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 O₃ 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 cm³/min. Note that this rate lies between the theoretically predicted rate, 24.5 cm³/min and the observed value, 18.1 ± 1.9 cm³/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)

<table>
<thead>
<tr>
<th>Level</th>
<th>O₃ Concentration (ppm)</th>
<th>Mean O₃ Mass Found, µg</th>
<th>N</th>
<th>Mean Sampling Rate**, cm³/min</th>
<th>SD</th>
<th>CV %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 × PEL</td>
<td>0.072</td>
<td>1.507</td>
<td>4</td>
<td>22.22</td>
<td>0.95</td>
<td>4.3</td>
</tr>
<tr>
<td>1 × PEL</td>
<td>0.118</td>
<td>2.676</td>
<td>7</td>
<td>24.06</td>
<td>3.39</td>
<td>14.1</td>
</tr>
<tr>
<td>2 × PEL</td>
<td>0.210</td>
<td>3.864</td>
<td>7</td>
<td>19.52</td>
<td>1.33</td>
<td>6.8</td>
</tr>
</tbody>
</table>

Average Sampling Rate = 21.93 ± 2.28 cm³/min

* Calculated from 1-L buret used as an exposure chamber (area section = 19.63 cm² or 0.021 ft²) and test atmosphere flow rate of 5 L/min through the chamber.

**Values calculated based on the following equation:

\[
\text{Sampling Rate (cc/min)} = \frac{\text{O}_3 \text{ found (µg) } \times 24.46 \times 1000}{\text{O}_3 \text{ Conc (ppm) } \times 47.997 \times \text{Sampling time (min)}}
\]

where: O₃ found (µg) = µg/mL, NO₃ × sampling volume, mL X GF
O₃ found (µg) = µg/mL, NO₃ × 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
Formaldehyde in Workplace Atmospheres  
(3M Model 3721 Monitor)

Related Information: Chemical Sampling - Formaldehyde

<table>
<thead>
<tr>
<th>Method no.:</th>
<th>ID-205</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix:</td>
<td>Air</td>
</tr>
</tbody>
</table>

OSHA Permissible Exposure  
Limit (PEL):  
1 ppm Time Weighted Average (TWA)*  
3 ppm Short-Term Exposure Limit (STEL)*

Collection Device:  
Passive badge monitor containing bisulfite-impregnated paper

Recommended Sampling Time:  
8 h (4 to 16 h range)

Average Sampling Rate:  
0.0614 ± 0.005 L/min (25 °C & 760 mmHg)

Face Velocity:  
Minimum 4.6 m/min (15 ft/min)

Analytical Procedure:  
A modified chromotropic acid procedure is used. Sample filters are desorbed using deionized water. Solutions are acidified, and chromotropic acid is added. The color complex formed is analyzed using a UV spectrophotometer at 580 nm.

Detection Limit  
Qualitative:  
0.039 ppm (4-h sampling time)  
Quantitative:  
0.11 ppm (4-h sampling time)

Dose Range:  
0.8 to 72 ppm-h (as claimed by the manufacturer)

Precision and Accuracy  
Validation Range:  
0.2 to 4.9 ppm  
CVt:  
0.084  
Bias**:  
+0.018  
Overall Error**:  
±18.6%

Method Classification:  
Validated Method

* The 3M Model 3721 monitor is recommended for TWA determinations only. It is not recommended for STEL monitoring. Any samples taken for STEL determinations should follow OSHA method No. 52.

** As compared to OSHA method no. ID-102.
Commercial manufacturers and products mentioned in this method are for descriptive use only and do not constitute endorsements by USDOL-OSHA. Although the following sampling procedure uses a specific formaldehyde monitor, other passive monitors can be substituted provided they meet validation requirements.

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

1. Introduction

This method describes the passive monitor collection of airborne formaldehyde in the breathing zone of workplace personnel and the subsequent analysis of those samples using a colorimetric technique. Although this method specifically mentions the 3M Model 3721 monitor, other monitors can be used provided performance requirements have been met. Some examples of validation procedures to determine performance are given in references 5.1. and 5.2.

1.1. History

The simplicity and freedom of the 3M Model 3751 formaldehyde passive monitor showed promise when first offered in 1981 as an industrial hygiene sampling alternative for formaldehyde (5.3.); however, subsequent independent studies indicated analyte loss when sampling at low humidities (5.4., 5.5.). Consequently, the Model 3751 monitor was removed from the market by 3M in April, 1984. The Model 3721 3M monitor, capable of sample humidification, was introduced in 1985 as a replacement. The changes instituted by 3M and incorporated into the model 3721 are:

1. A water-saturated pad in the bottom section of the monitor has been added for sample humidification.
2. Each monitor is now packaged in a sealed metal container. Previously, the Model 3751 monitor was enclosed in a resealable plastic bag.
3. The calculated sampling rate has been changed from 0.0659 to 0.0614 L/min.
   Note: The sampling rate of 0.0614 L/min is in agreement with a previous OSHA Salt Lake City Analytical Laboratory (SLCAL) study (5.5.).

With the exception of the moisturizing pad, the appearance of the Model 3721 is physically identical to the Model 3751 monitor. The Model 3751 monitor has been extensively evaluated by independent laboratories (5.4.-5.6.). Results from these studies did not indicate serious problems with desorption efficiency, face velocity, reverse diffusion, or post-collection sample storage stability. The recent modifications instituted by 3M suggest sampling performance would not be significantly affected in these areas. As long as the face velocity of the sampled environment is above 4.6 m/min (15 ft/min), the sampling rate of the monitor does not appear to be significantly altered (5.4.-5.7.). Sampling and analytical procedures are identical for either model monitor; however, result calculations are different since slightly different sampling rates are used.

1.2. Principle
The 3M formaldehyde monitor is a diffusion-type air monitoring assembly worn near the breathing zone of personnel to evaluate potential exposure to formaldehyde (HCHO) vapors. Formaldehyde vapor is adsorbed on bisulfite-impregnated paper located within the assembly. The resulting adduct is desorbed with deionized water. An aliquot of the sample is reacted with chromotropic acid in the presence of sulfuric acid to form a purple mono-cationic chromogen. The absorbance of this colored solution is read in a spectrophotometer at 580 nm and is compared to prepared standards. Although the chemistry of the color formation is not well-established, the following reaction mechanism is proposed in acidic solution (5.8.):

\[
\begin{align*}
\text{H}_2\text{SO}_4 & \quad \text{HCHO} \\
\text{C} & \quad \text{CH}_2 & \quad \text{C} \\
\text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH} \\
\end{align*}
\]

1.3. Advantages and Disadvantages

1.3.1. This method has adequate sensitivity for measuring workplace atmosphere concentrations of formaldehyde for TWA determinations.

1.3.2. The passive dosimeter used for collection of formaldehyde vapor is small, lightweight, and requires no sampling pumps.

1.3.3. The collected formaldehyde sample is stable for at least 30 days.

1.3.4. One disadvantage of the method is that the analytical procedure may not be capable of accurately determining STEL exposures at or below 3 ppm.

1.3.5. Another disadvantage with the dosimeter is sample rate dependence on face velocity. The dosimeter should not be used in areas where the air velocity is less than 4.6 m/min (15 ft/min). Most industrial work areas have air movement above 7.6 m/min (25 ft/min).

1.3.6. A disadvantage concerning the analytical procedure is the use of concentrated H\textsubscript{2}SO\textsubscript{4} during sample preparation. Extreme care should be used when handling H\textsubscript{2}SO\textsubscript{4}.

1.4. Method Performance (5.5., 5.9.)
1.4.1. This method was validated over the range of 0.2 to 4.9 ppm.

1.4.2. The coefficient of variation (CV,) for the total analytical and sampling method (50% RH) was 0.084. The overall error (as compared to the reference method OSHA ID-102) was ±18.6%.

1.4.3. The qualitative detection limit of the analytical method is 0.7 µg of formaldehyde based on a 3.0-mL sample volume. This is equivalent to 0.039 ppm for a 240-min sampling time.

1.4.4. The quantitative determination limit for the analytical method is 2 µg of formaldehyde in a 3.0-mL sample volume. This is equivalent to 0.11 ppm for a 240-min sampling time.

1.4.5. Somewhat variable results were obtained when sampling for a short duration (STEL). Therefore, the 3M Model 3721 monitor is recommended for 4 to 16-h sampling measurements only, and is not recommended for STEL sampling.

1.4.6. The Model 3751 monitor was extensively evaluated in 1982 (5.5.) and included storage stability, face velocity, sampling rate, and reverse diffusion experiments. Due to the similarity of the 3751 and 3721 monitors, these experiments were not repeated for the Model 3721. The 3751 experiments indicated (5.5.):

1. The results of a storage stability test show that the mean recovery of samples stored after 30 days were within ±10% of the mean of monitors analyzed immediately after sampling.
2. The results of a face velocity test indicate that the 3M Model 3751 monitor can accurately measure a known concentration as high as 10 ppm at face velocities as low as 15 ft/min.
3. The results of a sampling rate validation test indicate that the average sampling rate was 0.0614 ± 0.005 L/min.
4. The results of a reverse diffusion test indicate that reverse diffusion of collected formaldehyde from the monitor back into the atmosphere should not be a significant factor when sampling over an 8-h sampling period.

1.5. Interferences

1.5.1. When other substances are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

1.5.2. Any compound that has the potential of developing the same color as the formaldehyde/chromotropic acid complex using the conditions described in this method is an interference.

1.5.3. It has been reported by 3M that there is no interference from phenol (5.10.). The lack of interference is mainly due to the monitor's inability to collect a significant amount of phenol.

1.6. Uses (5.11.)

1.6.1. Formaldehyde (CAS 50-00-0) is used mainly as a raw material for producing synthetic resins. This accounts for over 50% of the total production of formaldehyde.

1.6.2. Potential occupational exposures to formaldehyde are listed:

- Anatomists
- Agricultural Workers
- Bakers
- Beauticians
- Biologists
- Botanists
- Glass etchers
- Glue and adhesive makers
- Grease-resistant textile finishers
- Greenhouse workers
- Hexamethylenetetramine makers
- Hide preservers
1.7. Physical Properties (5.11.):

Formula: HCHO
Molecular Weight: 30.03
Physical state: Gas
Melting point: -92 °C
Boiling point: -21 °C
Specific gravity: 0.815
Relative vapor density: 1.043 (air = 1)
Solubility: Soluble in water, alcohol, and ether
Color: Colorless
Odor: Pungent and irritating
Explosive limits (Gas): Gas 7.0–73% by volume in air
Flashpoint (closed cup): 50 °C (122 °F) of aqueous solution

1.8. Toxicology

Note: Information listed within this section is a synopsis of current knowledge of the physiological effects of formaldehyde (HCHO) and is not intended to be used as the basis for OSHA policy.

Formaldehyde is considered a strong irritant and potent sensitizer. Inhalation of large amount of HCHO can cause severe irritation of the upper respiratory tract and death. Data from human exposures indicate that exposure to large concentrations of HCHO gas may lead to pulmonary edema. Even HCHO gas present in the workroom at concentrations of 1 to 11 ppm can cause eye, nose, and throat irritation (5.11.). Formaldehyde has the potential to cause cancer in humans (5.12.).

The following symptoms have been noted in some individuals (5.12.):

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Symptoms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentration</td>
<td>Description</td>
</tr>
<tr>
<td>---------------</td>
<td>-------------</td>
</tr>
<tr>
<td>0.5 to 2 ppm</td>
<td>eyes, nose and throat irritation</td>
</tr>
<tr>
<td>3 to 5 ppm</td>
<td>tearing of the eyes</td>
</tr>
<tr>
<td>10 to 20 ppm</td>
<td>difficult breathing, nose and throat burning, cough, heavy tearing of the eyes</td>
</tr>
<tr>
<td>25 to 30 ppm</td>
<td>severe respiratory tract injury</td>
</tr>
<tr>
<td>100 ppm</td>
<td>immediately dangerous to life and health (IDLH)</td>
</tr>
</tbody>
</table>

2. Sampling

2.1. Precautions:

2.1.1. Avoid inhalation of or skin contact with formaldehyde.

2.1.2. If the possibility exists that the face velocity of an area being sampled is less than 4.6 m/min (15 ft/min), an active sampling device (i.e. OSHA sampling and analytical method No. 52) should be used instead of the passive monitor.

2.2. Equipment - Passive Monitors (If provided, also follow the 3M Formaldehyde Monitor Model 3721 - Instructions for Use.)

The 3M Model 3721 formaldehyde monitor (3M, St. Paul, MN) contains the following parts:

1) Container consisting of two aluminum cans held together by a label. The two cans are labeled can A and can B.
2) **Can A contains:**
   - Top Section (has a white film and plastic retaining ring),
   - Sealing Cup (has Date, Start Time, etc. written on it)
3) **Can B contains:**
   - Bottom Section (has a metal clip attached),
   - Translucent Closure Cap

Note: The original shipping container and aluminum cans can be reused for sample shipment to the lab.

2.2.1. Remove the plastic lid from can A. Open each can by grasping the ring tabs and carefully pulling up. Remove the lids from both cans. Examine the contents to make sure all parts are available.

2.2.2. Remove the Translucent Closure Cap from the Bottom Section. Save the Closure Cap.

2.2.3. Pressing firmly, snap together the Top and Bottom Sections. Make sure the white film and plastic ring are **NOT** removed from the Top Section. The monitor is now ready for sampling.

2.3. Sampling Procedure

2.3.1. Immediately begin sampling by attaching the monitor to the employee or by placing it in the sampling area. The white film (Top Section) should face away from the employee.

2.3.2. Record the following information:
1) Beginning sampling time
2) Sampling date
3) Monitor serial number
4) Employee or area identification
5) Temperature, pressure, and relative humidity at the sampling site

2.3.3. If possible, sample for 8 h. The minimum sampling time recommended is 1 to 2 h. For indoor air quality investigations, sample up to 16 h.

2.3.4. Immediately after sampling, remove and discard the white plastic film and purple retaining ring from the monitor. In place of the film/ring, snap on the Translucent Closure Cap by applying some pressure. A "clicking" sound should be heard when the cap is securely fastened.

2.3.5. Be sure both plugs on the Translucent Closure Cap are firmly seated. This will insure a gas-tight seal.

2.3.6. Snap the Sealing Cup into place on the Bottom Section of the monitor. Be sure the cup is snapped securely.

2.3.7. Record the end sampling time and any drastic change (>10%) in temperature, pressure, or relative humidity that may have occurred during sampling.

2.3.8. Assemble a blank sample in the same fashion as mentioned in Sections 2.2.1.-2.2.3. and 2.3.4.-2.3.6. Do not expose the blank.

2.4. Sample Shipment

2.4.1. Place each monitor back into the aluminum container, cover with the plastic cap, and securely wrap each can with an OSHA Form 21 sample seal.

2.4.2. Submit at least one blank sample with each set of samples. The blank sample should have been handled in the same manner as the other samples except that it was not exposed. If possible, also submit a "lot blank". This is an unused monitor inside an unopened aluminum container.

2.4.3. When other substances are known or suspected to be present in the air, such information should be transmitted with the sample.

2.4.4. Send the monitors directly to the laboratory and request formaldehyde analysis. The original shipping carton can be used for shipment.

3. Analysis

3.1. Precautions

3.1.1. Refer to instrument manuals for proper operation.

3.1.2. Observe laboratory safety regulations and practices.

3.1.3. CAUTION: Sulfuric acid can cause severe burns. Wear protective gloves, labcoat, and eyewear when handling concentrated sulfuric acid and the formaldehyde stock solution.

CAUTION: Formaldehyde has the potential to cause cancer in humans (5.12.). Extreme care must be observed when handling.

3.1.4. Do not store formaldehyde standards or samples in a refrigerator since polymerization will occur. Polymer precipitation may be observed by the appearance of a white milky substance in the formaldehyde solution.
3.1.5. Sodium sulfite solutions used for formaldehyde standardization gradually absorb carbon dioxide on exposure to air. Solutions which have stood for more than a week should be discarded.

3.1.6. Do not use reagent bottles having caps which contain phenolic resins. Formaldehyde contamination could occur.

3.2. Equipment

3.2.1. Spectrophotometer: double beam, 1-cm cell.

3.2.2. Meter, pH.

3.2.3. Miscellaneous volumetric glassware or plasticware: Volumetric burets, graduated cylinders, pipettes, volumetric and Erlenmeyer flasks, other laboratory glassware, syringes. (Note: All glassware or plasticware should be washed and rinsed thoroughly with deionized water and then air dried prior to use.)

3.2.4. Analytical balance (0.01 mg).

3.3. Reagents (All chemicals should be reagent grade or better.)

3.3.1. Deionized water (DI H$_2$O).

3.3.2. Chromotropic acid sodium salt (C$_{10}$H$_7$O$_8$S$_2$Na) solution (1%): Dissolve 1 g of chromotropic acid sodium salt (1,8-dihydroxy-3,6-naphthalenedisulfonic acid sodium salt) in 100 mL of DI H$_2$O. Prepare this solution daily. (Note: This reagent is also commonly referred to as 4,5-dihydroxy-2,7-naphthalenedisulfonic acid sodium salt)

3.3.3. Sulfuric acid (H$_2$SO$_4$), concentrated.

3.3.4. Sodium bisulfite (NaHSO$_3$), 1%: Dissolve 10 g of NaHSO$_3$ in 1 L of DI H$_2$O.

3.3.5. Formaldehyde (HCHO) solution, 37%.

3.3.6. Formaldehyde stock solution, ~1,000 g/mL: Dissolve 2.7 g (about 3 mL) of 37% HCHO solution in 1 L of DI H$_2$O. Standardize this solution as described in Section 3.4. The solution is stable for at least 6 months. (Note: After 6 months, the standardization should be repeated).

3.3.7. Reagents for standardization of HCHO stock solution:

1. Sodium carbonate (Na$_2$CO$_3$), certified, 99.9% minimum purity: Dry the Na$_2$CO$_3$ powder at 120 °C for 2 h, then transfer to a desiccator and cool to a constant weight. Use as a primary standard.
2. Sulfuric acid, 0.1 N: Dilute 3 mL of concentrated H$_2$SO$_4$ slowly to 1 L with DI H$_2$O.
3. Sodium sulfite (Na$_2$SO$_3$), 12.5% (W/V): Dissolve 140 g of anhydrous Na$_2$SO$_3$ in 980 mL DI H$_2$O. Store in a refrigerator (approximately 4 °C).

3.4. Standard Preparation

3.4.1. Standardization of the HCHO ~1,000 µg/mL stock solution (5.13., 5.14.):

1. Standardize the 0.1 N H$_2$SO$_4$ solution using the certified Na$_2$CO$_3$ as a primary standard: Weigh 1.00 to 1.20 g of dried Na$_2$CO$_3$ into a 250-mL beaker containing 50 mL of DI H$_2$O, add 3 drops of methyl red/bromocresol green indicator and titrate with the H$_2$SO$_4$ to a faint pink color. Heat the titrated solution to a gentle boil for 2 min to expel any dissolved CO$_2$, then cool the flask contents to room
temperature. If the end point has not been overrun, the indicator will reassume its characteristic green color. Complete the titration with H₂SO₄ to a sharp color change. Calculate the normality of the H₂SO₄ solution (N₂) based on the following equation:

\[ N_2 = \frac{\text{meq of Na₂CO₃}}{V_2} \]

Where:

\[ V_2 = \text{mL of H₂SO₄ solution required to titrate the Na₂CO₃.} \]

2. Use a pH meter and adjust the pH of 25.0 mL of the 12.5% Na₂SO₃ solution to 9.6 with the standardized 0.1 N H₂SO₄.

3. Place 50.0 mL of the HCHO ~1,000 µg/mL stock solution into a 250-mL beaker.

4. Add the previously adjusted Na₂SO₃ solution to the 250-mL beaker and titrate to a pH of 9.6 with the standardized 0.1 N H₂SO₄. Calculate the concentration of HCHO as follows:

\[
\frac{(A-B)(C)(D)}{E}
\]

\[ \text{HCHO, µg/mL} = \frac{(A-B)(C)(D)}{E} \]

Where:

A = mL of H₂SO₄ solution required to titrate the sample

B = mL of H₂SO₄ solution required to titrate the blank

C = normality of the H₂SO₄ solution (meq/mL)

D = (30 mg/meq of HCHO)(1,000 µg/mg)

\[ = 30 \times 10^3 \mu g/meq of HCHO \]

E = mL of formaldehyde used

3.4.2. Preparation of standards

To a series of 25-mL Erlenmeyer flasks already containing 2 mL of 1% NaHSO₃, carefully add 1.0, 3.0, 5.0, 10.0, 15.0, and 20.0 µL of the ~1,000 µg/mL HCHO stock solution. If the stock solution is prepared as exactly 1,000 µg/mL HCHO after standardization, these aliquots are equivalent to 1.0, 3.0, 5.0, 10.0, 15.0, and 20.0 µg of HCHO. As an alternative, standards can be prepared in 1% NaHSO₃ using serial dilution of the ~1,000 µg/mL stock solution.

3.5. Sample Preparation

3.5.1. Assemble and prepare a "lot blank" for analysis, if available (also see Section 2.4.2.).

3.5.2. Open both ports of the Translucent Closure Cap of each monitor.

3.5.3. Using the center port of the Translucent Closure Cap and a small pipette or syringe, add 3 mL of DI H₂O to each monitor. Reseal the ports.

3.5.4. After 30 min, with occasional gentle agitation, transfer a 2-mL aliquot of the solution into a 20-mL screw-cap glass vial and reserve for color development.
3.6. Analysis

3.6.1. Develop the color of samples, standards, and blank solutions by adding 1 mL of 1% chromotropic acid solution, and after thorough mixing, 5 mL of concentrated H$_2$SO$_4$.

(Note: Add the sulfuric acid slowly and carefully. Add H$_2$SO$_4$ to the samples and standards in the same fashion since heat catalyzes the color formation.)

3.6.2. Allow the solutions to cool to room temperature, then measure the absorbance of each solution at 580 nm using a 1-cm cell.

3.6.3. If the sample absorbance is larger than the absorbance of the highest standard, take a smaller aliquot from the monitor, dilute to 2 mL, and repeat Sections 3.6.1-3.6.2. Use the appropriate dilution factor in calculations if an aliquot other than 2 mL is taken.

3.7. Calculations

3.7.1. Use a least squares regression program to plot a concentration-response curve of peak absorbance versus the amount (µg) of formaldehyde in each standard.

3.7.2. Determine the amount (µg) of formaldehyde, A, corresponding to the absorbance in each analyzed sample aliquot from this curve.

3.7.3. Calculate the total amount (µg) of formaldehyde, W, in each sample:

\[
W = \frac{(A)\text{(sample vol, mL)}(DF)}{(\text{aliquot, mL})}
\]

Where:
DF = Dilution Factor (if none, DF = 1)

3.7.4. Blank correct each sample and calculate the concentration of formaldehyde in each sample:

\[
\text{ppm formaldehyde} = \frac{(W - W_b) \times MV}{MW \times (AV)}
\]

Where:
ST = Sampling time (min)
0.0614 = Sampling rate (L/min) at 25 °C and 760 mmHg
AV = ST × 0.0614 × (T1 / T2)$^{1.5}$ × (P2 / P1)
Wb = Total µg of formaldehyde in the blank sample
MV = Molar volume at 25 °C and 760 mmHg (24.45 L/mole)
MW = Molecular weight of formaldehyde (30 g/mole)
\[ T_1 = \text{Sampling site temperature (K)} \]
\[ T_2 = 298 \text{ K} \]
\[ P_1 = \text{Sampling site pressure (mmHg)} \]
\[ P_2 = 760 \text{ mmHg} \]

3.8. Reporting Results

Report results to the industrial hygienist as ppm formaldehyde.

4. Backup Report

See Reference 5.9. for complete information.

5. References


