Nitrogen Dioxide Operating Procedures

Air Quality Program

October 2003

03-02-19
# TABLE OF CONTENTS

1.0 **Introduction** ........................................................................................................... 1  
   1.1 Principle of Operation ..................................................................................... 1  

2.0 **Site Selection** ...................................................................................................... 1  
   2.1 The Monitoring Station .................................................................................. 2  
   2.2 Probe Placement ........................................................................................... 3  

3.0 **Routine Duties** .................................................................................................. 5  

4.0 **The Air Monitoring Instruments** ........................................................................ 6  
   4.1 Strip Chart Recorder ...................................................................................... 6  
   4.2 Sample Intake Line and Manifold ................................................................... 6  
   4.3 Gas Cylinder/Regulator .................................................................................. 7  
   4.4 The Analyzer .............................................................................................. 7  
   4.5 The Data Logger ........................................................................................... 9  
   4.6 The Gas Dilution System ............................................................................ 9  

5.0 **Instrument Calibration** ........................................................................................ 10  
   5.1 Manual Calibration Check ............................................................................. 10  
   5.2 Gas Phase Titration ........................................................................................ 14  
   5.3 Analyzer Adjustments ..................................................................................... 17  

6.0 **Precision** ............................................................................................................ 22  
   6.1 Manual Precision Check ................................................................................... 22  
   6.2 Daily Automated Precision Check .................................................................... 22  

7.0 **Maintenance** ....................................................................................................... 22  
   7.1 Inspection and Replacement of Sample Filter ................................................ 23  
   7.2 Inspect and Clean Fan Filters ........................................................................... 23  

8.0 **Quality Assurance** ............................................................................................. 23  
   8.1 Performance Audits ......................................................................................... 23  
   8.2 System Audits ............................................................................................... 23  

9.0 **Data Recording, Validating, and Reporting** ...................................................... 24  
   9.1 Precision .......................................................................................................... 24  
   9.2 Accuracy ........................................................................................................... 24  
   9.3 Data Completeness ......................................................................................... 24  

10.0 **Data Quality Assessment** .................................................................................. 24  

11.0 **References** ........................................................................................................ 24  

12.0 **Forms**

- Site Visit Checklist .................................................................................................................. 26
- Probe Inlet Siting Criteria Checklist for NO$_2$ ................................................................. 27
- Preventative Maintenance Schedule ...................................................................................... 28
1.0 Introduction

This procedure is intended for individuals responsible for collecting ambient air monitoring data supported by the Washington State Department of Ecology (Ecology).

The U.S. Environmental Protection Agency (EPA) has determined nitrogen dioxide (NO2) is a health and environmental concern. For this reason, National Ambient Air Quality Standards (NAAQS) have been established for nitrogen dioxide.

The objective of this procedure is to familiarize the station operator with procedures used in the collection of air monitoring data. The accuracy of data obtained from any instrument depends upon the instrument's performance and the operator's skill. It is important that the station operator become familiar with both this manual as well as the manufacturer's instruction manual in order to achieve a high level of data quality.

1.1 Principle of Operation

Concentrations of nitrogen dioxide in ambient air are determined indirectly by the chemiluminescent reaction of nitric oxide with ozone. Nitrogen dioxide is first quantitatively reduced to nitric oxide by a converter. The nitric oxide, which commonly exist in association with nitrogen dioxide, passes through the converter unchanged, resulting in a total nitrogen oxides (NOx) concentration of NO + NO2. A portion of the ambient air is also reacted with O3 without having passed through the converter, and the nitric oxide concentration measured. This value is subtracted from the NOx concentration yielding the concentration of NO2.

2.0 Site Selection

A primary objective of Ecology is to document where the highest long term NO2 averages may occur in the state. Major emission areas and wind patterns are determined (via special studies and modeling exercises) to select a monitoring site where potential maximum NO2 levels occur.

In selecting a site to monitor for NO2, factors that most affect site selection are:

- geographical distribution of population;
- location of pollutant emission sources;
- meteorology;
- topography.

In selecting a location to measure for NO2, it is important to understand that the reactive oxides of nitrogen in the atmosphere are primarily nitric oxide (NO) and nitrogen dioxide (NO2), known together as NOx. During the daytime, there is a rapid interconversion of NO and NO2. NO emitted into the air is converted to NO2 by photochemical reactions promoted by sunlight eventually creating
ozone downwind of the sources. The main sources of NOx are motor vehicles, power plants, industry, and outdoor burning. It is recommended that the station be located downwind of the expected point of maximum NOx to allow more time for the formation of NO2.

2.1 The Monitoring Station

In order for the monitoring equipment to perform at optimum, the structure housing the instruments must be clean, dry and temperature controlled.

Careful thought and planning is required in locating a monitoring station. The individual responsible for the installation must consider:

• **Proximity to the nearest power sources.** A 120 VAC source is required for operation of the NOX monitoring instruments.

• **Temperature.** The space where the equipment is housed must maintain a temperature range of 68 - 86 degrees F. This usually requires the need for an air conditioner and a heater controlled by a thermostat.

• **Accessibility of the equipment by the operator.** The operator must be able to safely access the equipment during regular business hours.

• **Security of the equipment.** Monitoring instruments are expensive. They must be placed in a location where security can be assured.

• **Contracts for rental of space or power.** Contracts need to be signed with the owner of the property where the instruments are to be located.

• **Telephone lines for data transmission to a central computer.** A four wire, dedicated 1200-baud telephone data line is needed to access the Ecology telemetry.

• **Local building codes.** In most cases, the contractor installing the power, structure, concrete, etc. will know the local building codes. The individual responsible for the installation should call the Public Works Department to inquire about the proposed plan and what is required.

• **Noise considerations.** It may be necessary to demonstrate how loud the instrument is before commitments are made.

• **Aesthetics of the monitoring station and sample probe.** An air monitoring shelter or a sampling probe attached to a building may be offensive or may not be allowed (i.e. historical buildings). It is a good idea to have photos or a diagram to explain the proposal.
2.2 Probe Placement

Once the location of the station has been identified, the individual responsible for the installation must be familiar with the probe siting criteria (see figure 2.1 Example of Siting Probe Criteria Checklist for NO$_2$). The location of the sample probe is critical and individuals performing the installation must follow specific guidelines involving:

- the distance of the probe inlet from nearby obstructions (buildings and trees);
- the vertical and horizontal distance of the probe inlet from the ground and support structure;
- the air flow around the inlet of the probe; and
- the distance of the probe inlet from nearby roads, parking lots, or any similar volume of automotive traffic.

<table>
<thead>
<tr>
<th>Scale</th>
<th>Height Above Ground in Meters</th>
<th>Distance From Supporting Structures in Meters</th>
<th>Other Spatial Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro</td>
<td>3 ± 1/2</td>
<td>≥ 1</td>
<td>1. Must be at least 10 meters from nearest intersection and should be at a mid-block location. 2. Must be at least 2 meters and no more than 10 meters from edge of nearest traffic lane. 3. Must have an unrestricted air flow of 270º around the inlet probe, or 180º if located on side of building</td>
</tr>
<tr>
<td>Middle and Neighborhoo</td>
<td>Between 3 and 15</td>
<td>≥ 1</td>
<td>1. Must have an unrestricted air flow of 270º around the inlet probe, or 180º if located on side of building. 2. Spacing from roads varies with traffic (see 40 CFR Part 58, Appendix E).</td>
</tr>
</tbody>
</table>

Figure 2.1
Sample Probe Inlet Siting Criteria Checklist for NO₂

Site #: 4100004A
Name: Olympic View
Address: 150 Duckabush Rd.
City: Pt. Discovery County: Jefferson

1. What is the vertical distance from ground to probe? 4 meters
   This distance must be between 3 and 15 meters.
   NOTE: The inlet probe must be located away from dirty, dusty areas.

2. Distance from support structure? This distance must be 2 meters greater than 1 meter. (This distance is in reference to walls, parapets or penthouses located on the roof).

3. Is there unrestricted air flow in an arc > 180° around the inlet probe? (If located on a building, the inlet probe should be on the windward side where the greatest pollutant concentration is expected.) YES X NO

4. What is the distance from the sample probe to nearby trees? 23 meters
   This distance should be greater than 20 meters from the drip line of the trees. If the trees act as an obstruction, the distance from the sample probe to the trees must be greater than 10 meters from the sample probe.

5. What is the distance from the inlet of the probe to the nearest obstacle? The distance from the obstacle, such as a building, must be at least twice the height the obstacle protrudes above the inlet probe. 20 meters

6. Distance from nearest road? Spacing from roads varies with traffic. (see 40 CPR Pt. 58, App.E, table 2). 50 meters

7. Comments: This monitoring station will start collecting data on April 1, 1995.

Completed by: Kim Barnett Date: 03-14-95
Agency: Jefferson County Air Authority

These guidelines often dictate the exact location of the air monitoring station. For new installations in the Ecology air-monitoring network, the Probe Siting Criteria Checklist
(figure 2.1) must be completed once the probe has been installed and the station is operational.

For specific information on siting criteria refer to Title 40, Code of Federal Regulations, Part 58 (40 CFR 58) and Washington State Department of Ecology, Air Quality Program, Site Selection and Installation Procedures.

3.0 Routine Duties

There are several routine duties that must be performed each time an air monitoring station is visited. These duties include equipment inspection, performing calibration checks, documentation, and making necessary adjustments or repairs to the instruments.

Once the operator has entered the monitoring station, she/he should first:

- Check for any obvious analyzer malfunctions. For example, check to see that the equipment is running, the pumps are operating and the instrument is cycling properly.

- Note any unusual odors or noise. An unusual odor may indicate a point source of a pollutant or a strange new noise can indicate a malfunction in the equipment. These observations should be recorded in the station logbook and may prove to be invaluable if the data is challenged.

Once the initial inspection is made, the operator must proceed with a routine inspection and perform a calibration check on the analyzer. To record what is done at the air monitoring station, a station logbook must be maintained at each monitoring site and should accurately reflect site operations. The logbook will be identified with the station name, station number, date, time, operator, instrument identification, parameter, scale and units. All entries shall include the date, time, quality control checks, and maintenance on equipment, audits, equipment changes and missing or invalid data. Additional information should include; maintenance performed on the station, abnormal traffic patterns, nearby construction and sample line cleaning. Should the data be challenged, the information recorded in the logbook is invaluable. Observations concerning abnormal operations or localized occurrences are critical if an exceedance of ambient air standards are recorded during this period. Completed logbooks must be sent to the Air Monitoring Coordinator at Ecology where they will be archived for future reference.

---


2 To obtain a copy of Site Selection and Installation Procedures contact the Washington State Department of Ecology, Air Program/QA Unit, P. O. Box 47600, P.O. Box 47600, Olympia, WA 98504-7600 (phone 206-407-6843).
4.0 The Air Monitoring Instruments

An air monitoring station designed to measure NO₂ in ambient air contains several instruments linked together to form a system that will analyze, record, and store the ambient air data. Once the structure to house the equipment is ready, the operator must obtain and install the instruments. The equipment includes:

- a NO/NOₓ/NO₂ analyzer that has been certified by the EPA as an equivalent reference method;
- a NO concentration standard traceable to a National Institute of Standards and Technology Standard Reference Material;
- a zero air source;
- a gas calibration system;
- a strip chart recorder;
- a data logger for the storage and transmitting of data;
- an electronic temperature sensor connected to the data logger to monitor the room temperature;
- the manufacturer's manuals for the instruments;
- FEP Teflon tubing for sampling line, 5/16 inch (outside diameter);
- a Teflon filter holder for the particulate filter;
- spare parts;
- extra chart paper, recorder pens, tape and scissors.

In order to collect the data and perform necessary maintenance on the equipment, the instruments should be arranged in the shelter in a configuration that provides for easy access by the station operator. The instruments must not be located against heaters or air conditioners as they may affect their performance.

4.1 Strip Chart Recorder

The strip chart recorder and the strip charts provide a graphical record of the analyzer performance. The instrument's signal output recorded by the data logger is averaged over a period of time and is often not a true representation of the quality of data collected. A data logger can mask noisy instrument output whereas the strip chart
would indicate the malfunction. Ecology uses several different types of recorders in
the air-monitoring network. The operator should have a manufacturer's manual for the
recorder at the monitoring station and follow the routine maintenance prescribed.

4.2 Sample Intake Line and Manifold

Ecology uses quarter inch (outside diameter) FEP Teflon tubing for the sample intake
line. It is important that the sample line be as short as possible and kept clean. No
matter how non-reactive the sample line material is initially, after a period of use
reactive particulate matter is deposited on the line walls. Dirt, insects, cobwebs, and
moisture can accumulate in the sample line and on the sample intake filter. It is the
responsibility of the operator to change the intake filter on a regular basis and to clean
or replace the sample line and manifold annually.

4.3 Gas Cylinder/Regulator

Operators will be required to replace the NO cylinder when the cylinder pressure drops
below 250 PSI. This will involve removing the regulator on the depleted cylinder and
installing the regulator on a replacement cylinder.

Precautions must be taken to remove "dead" pockets of contaminants which are created
within the regulator whenever it is removed from the cylinder. This problem can be
minimized by carefully evacuating the regulator (also known as purging) after it is
connected to the cylinder. Air trapped in the regulator can result in the NO converting
to NO₂ within the regulator resulting in errors during calibration. Better results will be
achieved by alternately pressurizing and depressurizing the regulator once it has been
attached to the cylinder. The operator is encouraged to contact Ecology's Air
Monitoring Unit for instructions on the proper method of regulator purging.

4.4 The Analyzer

The Ecology Air Monitoring network uses analyzers designed to measure the
concentration of nitric oxide, total oxides of nitrogen and, by calculation, nitrogen
dioxide. The analyzer measures the light intensity of the chemiluminescence gas phase
reaction of nitric oxide and ozone.

Atmospheric concentrations of NO₂ are measured indirectly by chemiluminescence by
first reducing the NO₂ to NO, then reacting the resultant NO with ozone and measuring
the light intensity from the reaction. In chemiluminescence NO₂ analyzers, the NO₂ in
a sample of air is first reduced to NO by means of a converter; any NO, which is
normally present in ambient air, passes through the converter unchanged causing a
resultant total NOₓ concentration equal to NO + NO₂. A portion of the air sample is
also reacted with O₃ without having passed through the converter. This latter NO
measurement is subtracted from the former measurement (NO + NO₂) to yield the final
NO₂ measurement.
Every analyzer comes with an operating and maintenance manual and must be kept with the analyzer at all times. The information contained in the manual contains instructions concerning:

- installing the analyzer;
- calibrating the analyzer;
- operating the analyzer;
- preventive maintenance schedule and procedures;
- troubleshooting; and
- expendable parts.

The manufacturer's manual is the best resource the station operator has for information on the operation of the analyzer. Troubleshooting tips can be found in the manufacturer's manual. It is strongly suggested that each station operator compile personal notes on troubleshooting as they gain experience with the instruments. If it appears that the field instrument will require major maintenance or repair that will last for several days, the operator must request a replacement instrument to prevent the loss of data over a long period of time.

The Thermo Environmental Instruments Model 42C NO/NO₂/NOₓ analyzer is used to sample for nitric oxides. Verify that the analyzer is operating and the ozonator is on. If the ozonator is not on, choose Instrument Controls from the Main Menu. From the Instrument Controls menu choose Ozonator. Press the ENTER pushbutton to turn the ozonator on. Press the RUN push button to return to the run screen.

4.5 The Data Logger

At all continuous air monitoring stations the ESC data logger is used to acquire, process, store and telemeter the air monitoring data to the central computer. No maintenance on the data logger is required but the station operator must contact the Telemetry Specialist in Lacey if a problem occurs.

To login to the data logger:
• press “ESC” key until Home Menu is displayed;
• select “L” Login on Home Menu <ENTER>;
• enter password “PRIV” <ENTER> ;

This will log you into the data logger and the Home Menu will be displayed.

4.6 The Gas Dilution System

Dasibi 5008 Programmable Multi-Gas Calibrator is used to generate gas concentrations of NO and NO₂. The calibrator has been designed to;

• provide an adequate flow and concentration range for the analyzer to be calibrated;
• have a stable ozone source with an adjustable output;
• have a reaction chamber residence time of less than two minutes;
• have a dynamic parameter specification of 2.75 PPM-minutes or greater at the operating conditions at which the calibration will be performed.

The Dasibi calibrator utilizes selection menus that the operator can navigate through. The operator can punch in the correct numbers, which correspond to preprogrammed levels. Each level is assigned a different concentration and type of gas.

5.0 Instrument Calibration

The purpose of the calibration is to determine the NO, NO₂ and NOₓ relationship between the analyzer and the true value of NO and NO₂ concentrations. This procedure involves the gas phase titration (GPT) of a NO standard with O₃ to produce NO₂. This method is based upon the rapid gas phase reaction between NO and O₃ to produce stoichiometric quantities of NO₂.

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

The calibration check is a quality control procedure used to verify that the air monitoring system is operating properly. The check involves comparing the response
of the station analyzer to NO-NO₂-NOₓ concentrations generated by the station gas calibration system.

The station operator is required to perform a manual calibration check once every fourteen days. Any adjustments to the analyzer should not be made until the calibration check is completed.

5.1 Manual Calibration Check

The Manual Calibration Check is a multi-point check of the analyzer to determine how the instrument is operating within the operating range of the instrument. This is determined by challenging the analyzer with a "true" gas concentration then calculating the deviation from the true value. If the difference is outside ± 10%, the cause for the error must be investigated, corrected and the calibration must be repeated. If the results of the calibration check exceed the 10% limit, the data recovered since the previous calibration check is subject to invalidation. The results are compared to subsequent calibration checks to detect possible analyzer drift or a change in the response. This procedure is described in 40 CFR 58, Appendix A and Quality Assurance Handbook for Air Pollution Measurement Systems, Volumes II and II.

Before beginning the calibration the analyzer must be in the auto mode. NO, NO₂ and NOₓ measurements should be displayed on the front panel. If the analyzer is not in the auto mode, choose Instrument Controls from the Main Menu. From the Instrument controls menu choose Auto/Manual Mode. Use the pushbutton to select auto mode (NO/NOₓ) and press ENTER. Press the RUN pushbutton to return to the Run screen.

Before performing a manual calibration check, mark the NO, NO₂, NOₓ channels off-line (out of service) by pressing a series of keys on the data logger;

- select the Configuration Menu “C” from Home Menu;
- select Configure (Data) Channels “D” from Configuration Menu;
- select Disable/Mark channel Off-line from Channel Configuration Menu;
- select channels to be marked off-line from list (01,02,04)<ENTER>;
- if additional channels are to be take off-line, select Disable/Mark channel Off-line from Channel Configuration Menu: from Channel configuration Menu press “ESC” key until Home Menu appears;
- select real-time Display Menu “D” from Home Menu;
- select Display Readings w/flags “F” from real-time Display Menu;
- out of this display verify that the above selected channel(s) are marked with “D” flag;
- Press “ESC” key to go back.

The manual calibration check involves the operator selecting pre-programmed gas levels stored by the Dasibi 5008 (calibrator). Each level corresponds to specific gas
concentrations that the calibrator has been programmed to generate. Once the calibrator has been setup and sent out to the air monitoring station, the majority of the interaction with the unit by the operator will involve selecting various levels from selection menus. These menus present a heading which describe the function or category of the functions available, followed by a numbered list of options. To begin a manual calibration check, the Main Menu must be displayed on the calibrator display.

To access the **Main Menu** press the **esc** button on the calibrator until the Main Menu is displayed.

Most of the interaction with the calibrator by the operator will make use of the **Control** and **Select Level** menus. The **Control** menu lists options that the operator can select to control the calibrator. To access the **Control** menu press the number 2 from the Main Menu, which will display the following menu:

<table>
<thead>
<tr>
<th>Time</th>
<th>Date</th>
<th>CONTROL</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:03:00</td>
<td>2/22/03</td>
<td>1: Select Level</td>
</tr>
<tr>
<td>AIR FLOW</td>
<td>.00 LPM</td>
<td>2: Start Sequence</td>
</tr>
<tr>
<td>GAS FLOW</td>
<td>.0 CCM</td>
<td>3: Manual Control</td>
</tr>
<tr>
<td>TOTAL</td>
<td>.00 LPM</td>
<td>4: Purge</td>
</tr>
<tr>
<td>O3 GEN</td>
<td>.00 %FS</td>
<td></td>
</tr>
<tr>
<td>O3 GAS</td>
<td>0 PPB</td>
<td></td>
</tr>
<tr>
<td>GAS</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To perform a calibration check, the operator must select a series of preprogrammed calibration levels using the **Select Level** menu. A list of the calibration levels can be found at the end of the procedures. To access the **Select Level** menu press the number 1 on the key pad resulting in the following menu:

Select the first calibration level by pressing the number 1 key. Press the **ent** key and the following menu will now be displayed:
The total flow rate is displayed for verification and an opportunity is given to abort the operation with the question *Are you sure?* Press the ‹ or ‡ button on the keypad until "Y" is displayed. Press the ent key to initiate zero air. Listen for the solenoid switch and the *Manual level started* message will be displayed followed by a new screen.

<table>
<thead>
<tr>
<th>Time</th>
<th>Date</th>
<th>Control:</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:05:00</td>
<td>2/22/03</td>
<td>1: Select Level</td>
</tr>
<tr>
<td>Air Flow</td>
<td>.00 LPM</td>
<td>2: Start Sequence</td>
</tr>
<tr>
<td>Gas Flow</td>
<td>.0 CCM</td>
<td>3: Manual Control</td>
</tr>
<tr>
<td>Total</td>
<td>.00 LPM</td>
<td>4: Purge</td>
</tr>
<tr>
<td>O3 Generator</td>
<td>.00 %FS</td>
<td></td>
</tr>
<tr>
<td>O3 Gas</td>
<td>0 PPB</td>
<td></td>
</tr>
<tr>
<td>Gas</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

On the left of the screen, the Status Display will display the air flow, gas flow, total flow, O₃ generator lamp intensity, O₃ gas and gas concentration.

Once initiated, zero air will be produced by the calibrator until terminated either via the stop command (by pressing number 4 under the Control menu), or by the initiation of another level or sequence. Once the calibrator begins to generate zero air, the operator should wait until a stable response is achieved and a good trace on the recorder is observed. This usually takes between 15-20 minutes. Record the analyzer value in the station logbook. Unless the zero has changed by more than ± 0.010 PPM, it is recommended that the zero not be adjusted. If an adjustment is needed, it should not be made until after the calibration check. To continue with the calibration check, esc back to the Main Menu and choose the Control Level and press 1: Select level.

Select the next calibration level by pressing the number 2 key. Press the ent key and the following menu will be displayed:
The Status Display will show the total flow rate for verification. The operator is now given the opportunity to review the flows before the calibration begins and is given the opportunity to cancel the operation with the question *Are you sure?* Press the ↑ or ↓ button on the keypad until "Y" is displayed. Press the ent key to initiate 450 PPB of NO. The gas flow and total flow will vary depending upon the concentration of gas in the NO cylinder. For demonstration purposes, a cylinder gas concentration of 50.0 PPM is used in calculating the gas and total flows.

Once the calibrator begins to generate a NO concentration of 450 PPB, the operator must wait until a stable response is achieved and the recorder trace plateaus. This usually takes between 15-20 minutes. Check to see that the data logger, analyzer display and recorder values match. Using the analyzer response from the data logger, calculate the percent difference using the following formula and record the results in the station logbook.

\[
\% \text{ Difference} = \frac{\text{Analyzer (data logger) - .450 ppm}}{.450 \text{ ppm}} \times 100
\]

On the calibrator, press 1: **Select Level.** The following information will now be displayed:

Select cal level 12 then press the ent key.

Select cal level 12 then press the ent key.
The total flow rate is displayed for verification and an opportunity is given to stop the operation with the question *Are you sure?* Make sure that the display reads 90 PPB of NO. Press the ↑ or ↓ button on the keypad until "Y" is displayed then press the **ent** key. Once the calibrator begins to generate 90 PPB of NO, wait until a stable response is achieved and a good trace on the recorder is observed. This usually takes between 15-20 minutes. Reading the analyzer response from the data logger, calculate the percent difference using the following equation and record the results in the station logbook.

\[
\text{% Difference} = \frac{\text{Analyzer (data logger)} - .090 \text{ PPM}}{.090 \text{ PPM}} \times 100
\]

### 5.3 Gas Phase Titration

The calibrator is designed to perform Gas Phase Titration (GPT) of NO with Ozone (O₃) to produce specified levels of nitric dioxide (NO₂).

The accuracy of an NO₂ calibration is directly related to the precision of ozone production by the calibrator. If a pure O₃ level of the same concentration as the desired NO₂ precedes a GPT, the calibrator will determine the correct lamp intensity required for that level under ambient conditions and the lamp intensity will be "locked in" for the subsequent GPT.

From the **Control** menu press the **1 : Select Level** on the keypad.

Select the next calibration level by pressing the number 71 key. Press the **ent** key and the following menu will now be displayed:
The total flow rate is displayed for verification and an opportunity is given to stop the operation with the question *Are you sure?* Press the ↑ or ↓ button on the keypad until "Y" is displayed. Press the *ent* key to initiate 400 PPB of O₃.

Since the analyzer does not measure ozone, the analyzer response will drop to near zero. It is critical that during this phase of the calibration that enough time is allowed for the calibrator to generate ozone. Usually this will take at least thirty minutes. The calibrator needs time to generate and measure the defined ozone concentration and "lock in" the lamp intensity. It is not necessary to record any values, just allow plenty of time for the calibrator to generate and measure 400 PPB of O₃. This can be observed on the left of the display screen. Once the calibrator has measured 400 PPB of O₃, return to the **Control** menu by pressing the 1 : **Select Level**.

Press the number 7 key followed by the *ent* key. The following menu will now be displayed:

Allow the calibrator to generate a NO₂ concentration of 400 PPB. The operator should wait until a stable response is achieved and the NO₂ trace plateaus on the recorder. This should take about forty minutes. Reading the analyzer response from the data logger, calculate the percent difference and record the results in the station logbook.

Return to the **Control menu** by pressing the 1 : **Select Level**.

Press the number 79 key followed by the *ent* key. The following menu will now be displayed:
Since the analyzer does not measure ozone, the analyzer response will drop to zero. It is critical that during this phase of the calibration, it is critical to let the calibrator generate ozone for at least thirty minutes. The calibrator needs time to generate and measure the defined ozone concentration and "lock in" the lamp intensity. It is not necessary to record any values, just allow plenty of time for the calibrator to generate and measure 90 PPB of O₃. This can be observed on the left of the display screen. Once the calibrator has measured 90 PPB of ozone, press 1: Select Level.

Press the number 11 key followed by the ent key. The following menu will now be displayed:

Allow the calibrator to generate a NO₂ concentration of 90 PPB. Wait until a stable response is achieved and allow twenty minutes for the NO₂ trace to plateau on the recorder. Read the analyzer response from the data logger. This response is the NO₂ Precision and the response must be recorded on the Precision Check Form and in the logbook. Calculate the percent difference using the following equation and record the results in the station logbook.

\[
\text{% Difference} = \frac{\text{Analyzer (data logger)} - .090 \text{ PPM}}{.090 \text{ PPM}} \times 100
\]

### 5.3 Analyzer Adjustments
The results of the calibration check will determine if an adjustment to the analyzer is needed. An adjustment to the analyzer may be needed if any of the calculations exceed \( \pm 7\% \) of the actual values. If any of the calculations exceed \( \pm 10\% \) of the actual values, the data will be suspect and may be invalidated. The operator must recalibrate the analyzer using the following procedures.

From the Select Menu on the Calibrator, select **cal level one**.

The total flow rate is displayed for verification and an opportunity is given to stop the operation with the question *Are you sure?* Press the ↑ or ↓ button on the keypad until "Y" is displayed. Press the **ent** key to initiate zero air.

**Allow the analyzer to sample zero air until stable NO, NO\(_x\), and NO\(_2\) responses are obtained.** After the responses have stabilized, from the MAIN MENU of the analyzer, choose the CALIBRATION menu displaying the following screen:

(Analyzer Screen)

From the Calibration menu select **Calibrate Zero** to display the following screen:
The Calibrate Zero screen displays the NO and NOx readings. Press ENTER to set the NO and NOx readings to zero. The message "SAVING PARAMETER (S)" is briefly displayed to indicate that the NO and NOx background readings have been set to zero.

From the Select Menu on the Calibrator, enter cal level 3, which will generate a NO concentration of 400 PPB.

Allow the analyzer to sample 400 PPB of NO until NO, NOx, and NO2 responses have stabilized and the trace plateaus for at least fifteen minutes. From the Main Menu of the analyzer choose CALIBRATION menu displaying the following screen:

Select CALIBRATE NO then Press enter:

The first line of the Calibrate NO screen displays the current NO reading. The second line of the display shows the current NO range. The third line of the display is where the NO calibration gas concentration is entered. Use the ← and → pushbuttons to move the cursor right and left and use the ↑ and ↓ pushbuttons to increment and decrement each digit. The NO should be set to 400.

Press the ENTER pushbutton to calibrate the NO channel to the NO calibration gas. The message "SAVING PARAMETER (S)" is briefly displayed to indicate that the NO
span coefficient has been calculated, stored, and is being used to correct the NO reading. The NO channel is now calibrated.

From the Main Menu of the analyzer choose the CALIBRATION menu displaying the following screen:

Select **CALIBRATE NOx** then Press enter:

The first line of the Calibrate NOx screen displays the current NOx reading. The second line of the display shows the current NOx range. The third line of the display is where the NOx calibration gas concentration is entered. Use the ← and → pushbuttons to move the cursor right and left and use the ↑ and ↓ pushbuttons to increment and decrement each digit. The NOx should be set to 400.

Press the **ENTER** pushbutton to calibrate the NOx channel. The message "SAVING PARAMETER(S)" is briefly displayed to indicate that the NOx span coefficient has been calculated, stored, and is being used to correct the NOx reading. The NOx channel is now calibrated.

From the Select Menu on the Calibrator, enter cal level 7 which will generate a NO₂ concentration of 400 PPB.
The total flow rate is displayed for verification and an opportunity is given to stop the operation with the question *Are you sure?* Press the ↑ or ↓ button on the keypad until "Y" is displayed. Press the **ent** key to initiate 400 PPB of NO₂.

Allow the analyzer to sample 400 PPB of NO₂ until NO, NOₓ, and NO₂ responses have stabilized and the trace plateaus for at least fifteen minutes. From the Main Menu of the analyzer choose CALIBRATION menu displaying the following screen:

Use the ↓ key to move the cursor down and select the **CALIBRATE NO₂** then press **Enter**:

The first line of the Calibrate NO₂ screen displays the current NO₂ reading. The second line of the display shows the current NO₂ range. The third line of the display is where the NO₂ calibration gas concentration is entered. Use the ← and → pushbuttons to move the cursor right and left and use the ↑ and ↓ pushbuttons to increment and decrement each digit. The NO₂ should be set to 400.

Press the **ENTER** pushbutton to calibrate the NO₂ channel. The message "SAVING PARAMETER (S)" is briefly displayed to indicate that the NO₂ span coefficient has been calculated, stored, and is being used to correct the NO₂ reading. The NO₂ channel is now calibrated.

The Model 42C does a one point NO₂ span coefficient calculation, corrects the NO₂ reading for converter inefficiency, and then adds the corrected NO₂ to the NO signal to give a corrected NOₓ signal. If the Model 42C calculates a NO₂ span coefficient of less that 0.96, either the entered NO₂ concentration is incorrect, the converter is not being heated to the proper temperature, the instruments needs servicing (leak or imbalance), or the converter needs replacement or servicing. Ecology's Technical Assistance Unit must be contacted to troubleshoot the problem.
Once the calibration check and maintenance has been completed, all channels which were previously disabled must be enabled. To do this:

- select Configuration Menu “C: from Home Menu;
- select configure (Data) Channels “D” from Configuration menu;
- select Enable/Mark Channel on-line “E" from Channel Configuration Menu;
- select channels to be marked on-line from the list then press <ENTER>

6.0 **Precision**

Precision is a data quality indicator used to determine how similar measurements are between two instruments. The precision results needs to be within a certain acceptable range in order for Ecology and EPA to make decisions with specified levels of confidence.

6.1 **Manual Precision Check**

The manual precision check is included in the calibration check the station operator performs every fourteen days. The operator records the actual values generated by the calibrator and the measured response of the analyzer at the precision level on the Ecology Air Monitoring Precision Check Form. The operator is required to send the form to the Quality Assurance Unit with the strip charts at the end of each month. For more detailed guidance refer to *Automated Method Data Documentation and Validation Procedures*.3

6.2 **Daily Automated Precision Check**

The station calibrator is preprogrammed to generate a two-point calibration every morning at 03:00 PST. The calibrator is programmed to generate zero air for fifteen minutes followed by a NO₂ concentration of 90 parts per billion (PPB) for thirty minutes. The calibration is followed by a purge cycle lasting for approximately fifteen minutes. The operator is strongly encouraged to check the daily calibration results from the telemetry each morning to verify that the instrument is operating properly. If there is a difference between the analyzer and the calibrator of ± 10%, the precision results are "flagged". It is the operator's responsibility to investigate why the calibration check failed.

7.0 **Maintenance**

---

3 To obtain a copy of *Automated Method Data Documentation and Validation Procedures*, contact Washington State Department of Ecology, Air Program/Quality Assurance Unit, P. O. Box 47600, Olympia, WA 98504-7600 (phone 206-407-6843).
Each instrument must be periodically examined and serviced to anticipate and prevent instrument failure. Scheduled maintenance on the instruments will prevent costly repairs and loss of data. The routine maintenance required on the analyzers by the station operator is minimal and is outlined in the manufacture's manual. By keeping track of the instrument responses from week to week, the operator can observe trends, which would alert the operator of a potential problem, and to correct the situation before the instrument fails. A preventative maintenance schedule is provided for the operator at the end of these procedures.

### 7.1 Inspection and Replacement of Sample Filter

The Teflon particulate filter in the Model 42C should be replaced monthly. The filter should have a 5 (or 2) micron pore size.

### 7.2 Inspect and Clean Fan Filters

Under normal use, the fan filters on the rear panel should be cleaned every six months. If the instrument is operated in excessively dirty surroundings, it may be necessary to clean the fan filters more frequently. Cleaning involves removing the two fan guards from the fans and flushing the filters with warm water. Once the filters have been allowed to dry, the filters and fan guards must be re-installed.

### 7.3 Probe Cleaning

If the sample probe is connected to a manifold, remove it from where it is connected to the manifold. Remove the sample line from the analyzer. Inject the sample line with small amounts of a commercial grade cleaner (i.e. Simple Green or Alconox) using an eye dropper or squeeze bottle. Blow the cleaner through the line with compressed air. Rinse the line several times with clean water.

### 7.4 Replacement for Air Feed Columns

Zero air is provided to the calibrator from an air compressor and a series of filter columns containing charcoal, soda lime, Purafil and DRIERITE. The charcoal, soda lime and Purafil need to be replaced once a year. The DRIERITE should be regenerated after it has turned from a dark blue to a light blue color.

DRIERITE is an all purpose drying agent for the efficient and rapid drying of air and can be regenerated many times for reuse. The granules may be spread in layers one granule deep and heated for one hour at 425º F. The regenerated material should be placed in the original glass or metal container and sealed while hot.

The temperature at which DRIERITE desiccants are regenerated is crucial in restoring DRIERITE to its original condition. Absorbed moisture is water of hydration and is chemically bound to the calcium sulfate of DRIERITE. Temperatures in the range of 400º - 450º F are required to break these bonds and release absorbed moisture. Lower
temperatures, regardless of heating time, will not regenerate DRIERITE. Care should be taken not to overheat DRIERITE as high temperatures can alter the crystal structure and render the desiccants permanently inactive.

8.0 Quality Assurance Audits

The accuracy of the data depends on how well operators follow procedures, operate equipment, collect the data and document their activities. Managers need to know how well things are going on their projects. An audit is a formal, detailed study of one or more aspects of a site or project by independent auditors.

8.1 Performance Audits

During each calendar quarter, utilizing the procedures and calculations specified in 40 CFR 58, Appendix A, "Quality Assurance Requirements for State and Local Air Monitoring Stations (SLAMS),” at least 25% of the automated analyzers will be audited.

8.2 System Audits

The systems audit is an on-site review and inspection of the entire ambient air monitoring program to assess its compliance with established regulations governing the collection, analysis, validation, and reporting of ambient air quality data. A systems audit will be performed annually by the Quality Assurance Coordinator. To provide uniformity in the evaluation, the criteria and procedures specified in EPA's Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, and Section 2.0.11 will be applied.

9.0 Data Recording, Validation and Reporting

For detailed information on handling, recordings, and validating air-monitoring data, refer to Ecology's Automated Method Data Documentation and Validation Procedures.

All data will be reviewed and certified by Quality Assurance prior to being reported or used to make decisions concerning air quality, air pollution abatement or control.

10.0 Data Quality Assessment

For each calendar quarter and year, Quality Assurance will prepare data precision, accuracy and completeness reports for the Program Manager and EPA.

10.1 Precision
The precision will be evaluated and reported employing the frequencies, procedures and
calculations in 40 CFR 58, Appendix A, "Quality Assurance Requirements for State and
Local Air Monitoring Stations (SLAMS)".

10.2 Accuracy

Using results from the performance audits and the calculations specified in 40 CFR 58,
Appendix A, "Quality Assurance Requirements for State and Local Air Monitoring
Stations". The accuracy will be evaluated and reported.

10.3 Data Completeness

The completeness of the data will be determined for each monitoring instrument and
expressed as a percentage. Percent valid data will be a gauge of the amount of valid
data obtained from the monitoring instrument, compared to the amount expected under
ideal conditions (24 hours per day, 365 days per year). Exceptions will be made for
analyzers that have a seasonal sampling period, which were not installed at the
beginning, or which were discontinued prior to the end of any reporting period for
calculation purposes.

11.0 References

1. Air Pollution Training Institute, Course 435 Atmospheric Sampling, Student Manual,

2. California Air Resources Board, Air Monitoring Quality Assurance Volume II,
Standard Operating Procedures for Air Quality Monitoring, Sacramento, CA.
1978.

3. Environmental Systems Corporation, ESC 8800 Data Logger Operation

4. Thermo Environmental Instruments Inc., Model 42C Instruction Manual,
Franklin, MA. 2000

5. Washington State Department of Ecology, Air Quality Program, Site Selection
and Installation Procedures, Lacey, WA. 1993.

Method Data Documentation and Validation Procedures, Lacey, WA. 1993.

7. Washington State Department of Ecology, Telemetry Regional Operational

### NO₂ MONITOR SITE VISIT CHECKLIST

<table>
<thead>
<tr>
<th>ITEMS TO BE CHECKED</th>
<th>Checked</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power on.</td>
<td></td>
</tr>
<tr>
<td>Pacific Standard Time (PST) noted on</td>
<td></td>
</tr>
<tr>
<td>Procedure</td>
<td>Description</td>
</tr>
<tr>
<td>---------------------------------------------------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Chart time correct.</td>
<td></td>
</tr>
<tr>
<td>Recorder chart pens replaced.</td>
<td></td>
</tr>
<tr>
<td>Adequate supply of nitric oxide gas.</td>
<td></td>
</tr>
<tr>
<td>NO$_2$, NO, NO$_x$ data logger channels disabled with date and time noted on chart.</td>
<td></td>
</tr>
<tr>
<td>Performed calibration check.</td>
<td></td>
</tr>
<tr>
<td>Chart, data logger, and analyzer read within .001 ppm of each other.</td>
<td></td>
</tr>
<tr>
<td>Adjustments made following calibration check.</td>
<td></td>
</tr>
<tr>
<td>Sample filter replaced.</td>
<td></td>
</tr>
<tr>
<td>Fan filter inspected.</td>
<td></td>
</tr>
<tr>
<td>Silica gel, charcoal replaced.</td>
<td></td>
</tr>
<tr>
<td>Chart paper replaced</td>
<td></td>
</tr>
<tr>
<td>Following a calibration and maintenance, analyzer switched to remote mode.</td>
<td></td>
</tr>
<tr>
<td>NO$_2$, NO, NO$_x$ data logger channels enabled with date and time noted on chart.</td>
<td></td>
</tr>
</tbody>
</table>

### Probe Inlet Siting Criteria Checklist for NO$_2$

- **Site #:**
- **Name:**
- **Address:**
1. What is the vertical distance from ground to probe?
   This distance must be greater than 3-15 meters.
   NOTE: The inlet probe must be located away from dirty, dusty areas.

2. Distance from support structure? This distance must be greater than 1 meter. (This distance is in reference to walls, parapets or penthouses located on the roof).

3. Is there unrestricted air flow in an arc > 180° around the inlet probe? (If located on a building, the inlet probe should be on the windward side where the greatest pollutant concentration is expected.)

4. What is the distance from the sample probe to nearby trees?
   This distance should be greater than 20 meters from the drip line of the trees. If the trees act as an obstruction, the distance from the sample probe to the trees must be greater than 10 meters from the sample probe.

5. What is the distance from the inlet of the probe to the nearest obstacle? The distance from the obstacle, such as a building, must be at least twice the height the obstacle protrudes above the inlet probe.

6. Distance from nearest road? Spacing from roads varies with traffic. (see 40 CPR Pt. 58, App.E, table 2).

7. Comments: ___________________________________________________________

Completed by: ___________________________ Date: ___________________________

Agency: ________________________________________________________________
**THERMO ENVIRONMENTAL INSTRUMENTS INC. 42C PREVENTATIVE MAINTENANCE SCHEDULE**

<table>
<thead>
<tr>
<th>Maintenance Detail</th>
<th>Manual Reference</th>
<th>JAN</th>
<th>FEB</th>
<th>MAR</th>
<th>APR</th>
<th>MAY</th>
<th>JUN</th>
<th>JUL</th>
<th>AUG</th>
<th>SEP</th>
<th>OCT</th>
<th>NOV</th>
<th>DEC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>At every site visit,</strong> check the silica gel (dark blue). Replace it when the color changes to light blue.</td>
<td>5.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Every month,</strong> inspect and replace the sample filter.</td>
<td>5.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Every month,</strong> Inspect the fan filters. Clean the filters with warm water.</td>
<td>5.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Every year,</strong> clean the probe or replace with new tubing.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**ANALYZER STATE TAG #**

**OPERATOR:**

Note: Record the day of the month each task was completed