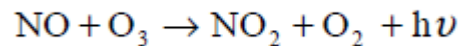


## 1.0 Introduction

Scientific Principle:

The NO<sub>x</sub> analyzer principle is based on nitric oxide (NO) and ozone (O<sub>3</sub>) react to produce a characteristic luminescence with intensity linearly proportional to the NO concentration. Infrared light emission results when electronically excited NO<sub>2</sub> molecules decay to lower energy states. Specifically,



Nitrogen dioxide (NO<sub>2</sub>) must first be transformed into NO before it can be measured using the chemiluminescent reaction. NO<sub>2</sub> is converted to NO by a stainless steel NO<sub>2</sub> to NO converter heated to about 625°C (the optional molybdenum converter is heated to 325°C).

The sample is drawn in through the sample bulkhead, then the sample flows through a capillary to the mode valve. The mode valve routes the sample either directly to the reaction chamber (NO mode) or through the NO<sub>2</sub> to NO converter and then to the reaction chamber (NO<sub>x</sub> mode). Dry air enters through the dry air bulkhead, through a flow switch, and then through a silent discharge ozonator. The ozonator produces the ozone required for the chemiluminescent reaction. The ozone reacts with the NO in the ambient air sample to produce electronically excited NO<sub>2</sub> molecules. A photomultiplier tube (PMT) housed in a thermoelectric cooler detects the NO<sub>2</sub> luminescence. From the PMT, the exhaust travel through the ozone (O<sub>3</sub>) converter to the pump, and is released through the vent. The NO and NO<sub>x</sub> concentrations calculated in the NO and NO<sub>x</sub> modes are stored in memory. The difference between the concentrations is used to calculate the NO<sub>2</sub> concentration. The analyzer outputs NO, NO<sub>2</sub>, and NO<sub>x</sub> concentrations to both the front panel display and the analog outputs.

## 2.0 Applicability and Use

- To obtain timely data for the purpose of air quality assessment
- air quality trend reporting
- meet the requirements for inclusion of data in provincial and national air quality databases
- A continuous method of monitoring hydrogen sulphide concentrations in ambient air

This method is capable of measurement updates at a rate of once every minute. This method captures and records H<sub>2</sub>S readings every minute, and one minute readings are compiled in to one hour averages.



## 2.1 Range

This method is applicable to the measurement of NO, NO<sub>2</sub> and NO<sub>x</sub> concentrations in ambient air in the range of 0-500 or 0-1000 parts per billion.

This method adheres to the requirements of the current Air Monitoring Directive (AMD) drafted by Alberta Environment in 1989. In some cases the limits and specifications exceed the requirements of the current AMD and subsequent amendments. It should be considered that the current and any future amendments or drafts of the AMD will be used as the benchmark for requirements and criteria for ambient air monitoring practices conducted in the Province of Alberta.

## 3.0 Additional References

- Alberta Air Monitoring Directive 1989
- 2006 Amendment to the 1989 Alberta Air Monitoring Directive

## 4.0 Precision and Accuracy

The measurement precision is generally considered to be the “repeatability of the measurement”. Precision of the data output by the analyzer is established by the manufacturer, but confirmed during daily and monthly calibration checks.

The accuracy of the analyzer is generally considered the “deviation from true”. This means how close it is to what it should be. The benchmark of “what it should be” is provided by the Alberta Environment audit team and the use of transfer standards from the National Institute of Standards and Technology (NIST). As with precision, accuracy is confirmed by the daily and monthly calibration checks.

The accuracy and precision of the analyzer are specified by the manufacturer in the instrument manual.

### 4.1 Reporting Detection Limits

The NO<sub>x</sub> analyzers used in this method are commercially available models. The measurement range, depending on the manufacturer make and model, is highly variable. The typical range selection used in Alberta for ambient air monitoring is either 0-500 ppb or 0-1000 ppb.

Data generated from these analyzers are reported to the nearest 0.001ppb

## 5.0 Setup and Operation

All the installation requirements are specified by the manufacturer in the installation procedures of the manual. General requirements listed below must also be followed.

- The ¼ inch diameter connection tubing from the manifold to the analyzer inlet must be made of Teflon or equivalent material for chemical inertness. These lines should be kept as short as possible to keep residence time of the sample flow to a minimum.
- A charcoal scrubber must be installed upstream of the pump to prevent ozone from corroding the pump diaphragm
- A particulate filter, made of material that does not absorb hydrogen sulphide, with a pore size of no larger than 5.0µm must be placed in the sampling line before the sample enters the analyzer. The filter is to be located as close as possible to the manifold inlet. The holder for the filter will be made of Teflon or stainless steel.
- A data acquisition system will be connected to the analyzer to record the signal output from the analyzer. For connection to record analog voltage signals, the system will be set to match the voltage range of the analyzer output. Generally this is 10V full scale.
- The monitoring station temperature will be controlled within the range of 20 to 25°C. It is important to note that the analyzer will operate properly at any temperature within this range; however, stability of the station temperature will yield more representative data.
- The monthly multi-point calibration gas is introduced to analyzer upstream the sample filter. The sample inlet filter is changed before the calibration is performed.
- Necessary channels must be put into "Maintenance" before calibration/maintenance starts.

## 6.0 Calibration Procedure

Below is the procedure used to calibrate the analyzer for the monthly multi-point calibration. The procedure described below applies to all three channels of the analyzer.

The total flow of any calibration point generated by the calibrator must be at minimum, a factor of 2.5 greater than the flow demand of the analyzer. All calibrations require the sample line from the calibrator to the analyzer have a positive pressure bypass in order to deliver gas to the analyzer at the pressure required by the analyzer.

1. Initiate flow of a zero-air gas to the analyzer. Record the "Diluent and Cal Gas" flow rates.
2. After the monitor reading has stabilized for 20 minutes, record the resultant unadjusted zero reading as "as found zero".
3. The operator will then adjust the zero unless the "as found zero" is not 0.000.
4. After the adjusted monitor reading has stabilized for 20 minutes, record the resultant adjusted zero reading as "adjusted zero".



5. Initiate a flow of a known gas between 50% and 80% of the full scale to the analyzer. Record the "Diluent Flow Rate" and "Cal Gas Flow Rate". Determine the Calculated concentration (CC) (refer to 8.1-a).
6. After the monitor reading has stabilized for 20 minutes, record the resultant unadjusted reading as "as found high". Calculate the correction factor (CF) (refer to 8.1-b).
7. The analyzer will then be adjusted in accordance with the analyzer manufacturer's procedures to give a correction factor as close to 1.000 as possible. If CF is outside +/-15%, an explanation must be given along with corrective actions followed by re-calibration the analyzer (repeat 6.0).
8. After the adjusted monitor reading has stabilized for 20 minutes, record the resultant adjusted reading as "adjusted high". Calculate and record. Calculate the correction factor (CF). (refer to 8.1b). Correction factor must be as close to 1.000 as possible.
9. Initiate a flow of a known gas between 25% and 40% of the full scale range. After the monitor reading has stabilized for 20 minutes, record the resultant instrument reading. Calculate the correction factor (CF) (refer to 8.1-b). Correction factor must be 0.95 to 1.05.
10. Initiate a flow of a known gas between 10% and 20% of the full scale range. After the monitor reading has stabilized for 20 minutes, record the resultant instrument reading. Calculate the correction factor (CF) (refer to 8.1-b). Correction factor must be 0.95 to 1.05.
11. Initiate flow of a zero-air gas through the analyzer. After the monitor reading has stabilized 20 minutes, record the resultant instrument reading. If the resultant instrument reading is outside of +/-3% of the analyzer full scale, the calibration is to be repeated. (repeat 6.0).
12. Reintroduce the highest NO concentration which was generated in the NO portion of the calibration. Allow 20 minutes for the analyzer to stabilize.
13. On the calibrator, ozone is introduced by selecting an ozonator lamp voltage or concentration that produces a concentration of ozone that is between 60% and 75% of the high NO point. This is the "as found" for calibration of the NO<sub>2</sub> channel. Allow for 20 minutes of stabilization.
14. The analyzer's NO<sub>2</sub> output is adjusted (NO<sub>2</sub> only, NO and NO<sub>x</sub> CANNOT BE ADJUSTED), as per the manufacturer's procedure to give an NO<sub>2</sub> correction factor as close to 1.000 as possible. Once a stable reading (20 minutes) is achieved. Record the resultant NO, NO<sub>x</sub>, NO<sub>2</sub> readings.
15. Ozone is then introduced by selecting an ozonator lamp voltage or concentration that produces a concentration of ozone that is between 25% and 40% of the high NO point. This is the mid-point for calibration of the NO<sub>2</sub> channel. No adjustment is made to the analyzer output for this point. After the monitor readings have stabilized (20 minutes), record the resultant NO, NO<sub>x</sub>, NO<sub>2</sub> readings.
16. Ozone is lastly introduced by selecting an ozonator lamp voltage or concentration that produces a concentration of ozone that is between 10% and 20% of the NO gas concentration is converted to NO<sub>2</sub>. This is the third and low-point for calibration of the NO<sub>2</sub> channel. No adjustment is made to the analyzer output for this point. After the monitor readings have stabilized (20 minutes), record the resultant NO, NO<sub>x</sub>, NO<sub>2</sub> readings.
17. Plot the NO<sub>2</sub> increase versus the NO decrease to produce a calibration curve. Maximum deviation of any point from the slop of the graph must not exceed 5%.
18. The average convertor efficiency for the calibration must then be calculated and recorded.



19. Calculate the average converter efficiency by summing the converter efficiencies for each point and dividing this result by the number of GPT points (refer to 8.1-d). If converter efficiency is less than 85% corrective action must be taken and the analyzer recalibrated.
20. Turn off the U.V. lamp in the calibrator.
21. Initiate the analyzers auto zero/span sequence and record the resultant instrument readings for each.

## 7.0 Quality Control Requirements

Below are the requirements for the daily zero and span to ensure proper analyzer operation.

<b>Slope</b>	<b>0.85 to 1.15</b>
<b>Intercept</b>	<b>&lt; 3 % of full scale</b>
<b>Correlation Coefficient</b>	<b>&gt;0.995</b>
<b>Converter Efficiency</b>	<b>&gt;85%</b>

If any of the above criteria are not met, the analyzer is considered to be non-linear. Determination as to why the calibration was not successful followed by repair and re-calibration must be made immediately. The calibration records must document why the initial calibration was not successful.

## 8.0 Data Calculation and Reporting

### 8.1 Calculations

- a. Calculated Concentration (C.C.)

$$C.C. = \frac{(Source\ Gas\ Flow\ Rate\ \times\ Cal\ Gas\ Concentration)}{(Source\ Gas\ Flow\ Rate\ +\ Dilution\ Air\ Flow\ Rate)} \times 1000$$

Unit: ppm or ppb

- b. Correction Factor (C.F.)



$$\text{C.F.} = \frac{\text{Calculated Concentration}}{\text{Indicated Concentration}}$$

Unit: %

c. Percent Different(P.D.)

$$\text{P.D.} = \frac{(\text{C.F. after adj. span previous month} - \text{C.F. before span adj. current month})}{\text{C.F. before span adj. current month}} \times 100$$

Unit:%

d. Converter Efficiency (C.E.)

$$\text{C.E.} = \frac{1}{\text{Average C.F. of three GPT points}} \times 100$$

Unit:%

## 8.2 Reporting

All internal operating parameters of the analyzer are to be entered in the calibration spreadsheet. The station log book is to be updated with:

- Date of the calibration
- Any irregularities during the calibration along with an explanation
- Analyzer change out along with an explanation why