

1.0 Introduction

Ozone analyzers operate on the principle that ozone (O₃) molecules absorb UV light at a wavelength of 254 nm. The degree to which the UV light is absorbed is directly related to the ozone concentration as described by the Beer-Lambert Law.

The sample is drawn in to the sample bulkhead and is split into two gas streams. One gas stream flows through an ozone scrubber to become the reference gas. The reference gas then flows to the reference solenoid valve. The sample gas flows directly to the sample solenoid valve. The solenoid valves alternate the reference and sample gas streams between cells A and B every 10 seconds. When cell A contains reference gas, cell B contains sample gas and vice versa. The UV light intensities of each cell are measured by detectors A and B. When the solenoid valves switch the reference and sample gas streams to opposite cells, the light intensities are ignored for several seconds to allow the cells to be flushed. The analyzer calculates the ozone concentration for each cell and outputs the average concentration to the front panel display, the analog outputs, and also makes the data available over the serial or ethernet connection.

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 ozone concentrations in ambient air

This method is capable of measurement updates at a rate of once every minute. This method captures and records ozone 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 ozone concentrations in ambient air in the range of 500 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 ozone 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 0 to 500 ppb.

Data generated from these analyzers are reported to the nearest 0.1 ppb.

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 particulate filter, made of material that does not absorb ozone, 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 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.

Prior to commencement of the ozone calibration a full GPT NO₂ calibration must be performed within the previous 24 hour period to attain the proper ozone concentration outputs for the settings used.

The NO drop of each GPT is to be copied and pasted in to the ozone calibration form. The exact settings used from the GPT calibration will be used to generate the ozone output, except the NO calibration gas cannot be used since it will react with and eradicate a large portion of the ozone generated for the ozone calibration.

Note that the total flow MUST be the same for the identical ozone points to be generated. For example, if the high GPT point used 5000 cc/min of dilution air and 80cc/min of calibration gas with an ozone lamp setting of 400 ppb, then for the ozone calibration, the flows would be 5080 cc/min of dilution flow, 0cc/min calibration gas flow with a lamp setting of 400 ppb.

- a. Initiate flow of a zero-air gas to the analyzer. Record the "Diluent" flow rate. Be sure to add additional diluent flow so the total flow is the same as the total flow in the equivalent GPT point from the NO₂ calibration.
- b. After the monitor reading has stabilized for 20 minutes, record the resultant unadjusted zero reading as "as found zero".
- c. The operator will then adjust the zero unless the "as found zero" is not 0.000.



- d. After the adjusted monitor reading has stabilized for 20 minutes, record the resultant adjusted zero reading as "adjusted zero".
- e. Initiate the high point using the same settings as the GPT high point. This should be between 50% and 80% of the full scale to the analyzer. Record the "Diluent Flow Rate". Calculated concentration for ozone must be the same as the NO drop in the GPT high point.
- f. 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-a). The analyzer will then be adjusted in accordance with the analyzer manufacturers 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).
- g. 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 8.1a). Correction factor must be as close to 1.000 as possible.
- h. Initiate the mid-point using the same settings as the GPT mid-point. This should be between 25% and 40% of the full scale to the analyzer. Record the "Diluent Flow Rate". Calculated concentration for ozone must be the same as the NO drop in the GPT mid-point. After the monitor reading has stabilized for 20 minutes, record the resultant instrument reading. Calculate the correction factor (CF) (refer to 8.1-a). Correction factor must be 0.95 to 1.05.
- i. Initiate the low-point using the same settings as the GPT low-point. This should be between 10% and 20% of the full scale to the analyzer. Record the "Diluent Flow Rate". Calculated concentration for ozone must be the same as the NO drop in the GPT low-point. After the monitor reading has stabilized for 20 minutes, record the resultant instrument reading. Calculate the correction factor (CF) (refer to 8.1-a). Correction factor must be 0.95 to 1.05.
- j. 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).
- k. Initiate the analyzer auto zero/span sequence and record the resultant instrument readings for each, and record the new expected value, and input this value in to the logger.
- l. Calculate the average correction factor and record.
- m. Calculate the percent change from the previous calibration (PD) (refer to 8.1-b). Percent change must be < 15%.

7.0 Quality Control Requirements

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

Slope	0.85 to 1.15
Intercept	< 3 % of full scale
Correlation Coefficient	>0.995



Percent Change	< 15%
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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. Correction Factor (C.F.)

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

Unit: None

b. 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:%



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