WBEA – Standard Operating Procedure

SOP Title	**Procedures for operating continuous Ozone (O3) analyzers**
SOP Number	**WBEA SOP-ANA-006 O3**
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Revision History

Revision #	Date	Description	Author

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Table of Contents

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Introduction and Background

This document is intended to be used as a reference for use in the calibration, maintenance and operation of continuous analysis of ozone in ambient air. The proper utilization of this procedure in conjunction with the operators manual will conform to the current Alberta Air Monitoring Directive (AMD) and enable the data to be included in provincial and national air quality data bases

Principle of the Method

The method uses the principle of ultra violet (UV) light absorption of the ozone molecule at the wavelength of 254 nm. By knowing the absorption coefficient of ozone, geometry of the measurement cell, and the pressure and temperature of the air sample, the concentration of the ozone in the sample can be determined by the transmittance of UV light through the measurement cell. The quantities are related to the Beer-Lambert Law. (Lodge. 1991. “Methods of Air Sampling and Analysis”, 3rd edition. *p.422*), (“Technical Assistance Document for the Calibration of Ambient Ozone Monitors”. EPA/600/4-79-057, September 1979, United States Environment Protection Agency, Research Triangle Park, NC 27711).

Ambient air is drawn through the instrument by a pump at the exit end of the flow path. The sample air is scrubbed of ozone by passing through an ozone scrubber. This ozone free air sample is passed through the measurement cell and the intensity of the UV light is measured by a stabilized photo detector. The other part of the measurement cycle allows the sample air to pass directly through to the measurement cell unaltered. The intensity of the UV light will be partially absorbed by the presence of ozone molecules in the sample. By comparing the difference in the UV transmittance of scrubbed and unaltered air the concentration of ozone in the air sample can be quantified.

Measurement Range and Sensitivity

The ozone analyzers used in this method are commercially available models. The measurement range is user selectable at ranges between 0 to 1000 parts per billion by volume (ppb). The typical range selection used in the WBEA network is 0 to 500 ppb.

The detection limit of the analyzer is specified by the manufacturer and specific settings applied to the analyzer when placed in the field. This is also governed by the noise level of the output signal, whether analog or digital. Two times the noise level is generally accepted as the lower detectable limit (LDL). Generally it is at the 1.0 ppb level. The health of the analyzer is important as poor health = higher noise = higher LDL.

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Equipment and Apparatus

Ozone analyzers used in the WBEA network include:

- Thermo Environmental Instruments – model 49C and 49i analyzers
- Teledyne API – model 400A analyzer

Both of these makes are EPA designated analyzers and data produced from these instruments is accepted by all agencies.

This does not exclude the use of other equipment that has received the USEPA Reference and Equivalent Method designation; however none are currently used in the WBEA network.

Interferences

At concentration levels normally encountered in urban ambient air, gaseous compounds such as nitrogen dioxide, sulphur dioxide and volatile organic compounds (VOC) have negligible effect on the accuracy of the measurement.

Any other gas in the air sample that also absorbs at a wavelength of 254 nm (ie Aromatic hydrocarbons, mercury) could present interference. The UV analyzer operates by comparing absorption measurements of the sample air with measurements of the same sample air after removal of only the ozone by an ozone scrubber. Ideally, a gas that absorbs at 254 nm will do so equally in both measurements, and the effect will cancel. The scrubber must remove 100% of the ozone while quantitatively passing other gases that absorb at 254 nm. Some gases, however, may be partially or temporarily absorbed or adsorbed by the scrubber, such that their concentration is not equal in both measurements. An interference can occur when a gas absorbs at 254 nm or produces some other physical effect (such as water condensing on scratches in the cell window), and does not pass freely through the ozone scrubber. Hence, proper scrubber performance is critical to minimizing interferences.

Particulate matter present in the measurement cell will interfere with UV absorption measurement by either scattering and or absorption of the instance beam. This problem is normally eliminated by using a particle filter of 5.0µm pore size made of inert material, such as Teflon, at the sample inlet of the instrument.

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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 sensor 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 Program staff and the use of high quality transfer standards such as available from the National Institute of Standards and Technology (NIST). As with precision, accuracy is confirmed by the daily span and monthly calibration checks.

Site Requirements

All O_3 analyzers are housed in a temperature controlled ambient air monitoring shelter in a standard instrument rack. Sample air is brought into the shelter using a glass sample inlet system and made available to the O_3 analyzer. The station is sited according to appendix A-2, Station Site Criteria section of the AMD. Site location for O_3 monitoring should be determined according to the intended application of the monitoring data.

Detailed requirements for selection of sites for monitoring ambient ozone for the Canada Wide Standard (CWS) determination can be found in “Guidance Document on Achievement Determination- Canada Wide Standards for Particulate Matter and Ozone section 3.0.

Installation Requirements

All the installation requirements as specified by the manufacturer in the installation procedures as well as the general requirements below must be followed.

- The ¼ inch outside diameter (inside diameter of 3/16 inch or 1/8 inch) connection tubing from the manifold to the analyzer inlet must be made of Teflon or equivalent material for chemical inertness to the ozone sample. The line should be kept as short as possible and must not exceed 10 meters in length.
- An entirely Teflon particulate filter membrane (Pall Scientific Zeflour or equivalent) with a pore size of no larger than 5.0µm must be placed in the sampling line before the air sample enters the detection cells and is recommended to be located as close as possible to the inlet manifold. The holder for such filter must also be made of Teflon, or Delrin.

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- A data acquisition system (DAS) should be connected to the analyzer to record or download the signal output from the analyzer. For connection to record analog voltage signals, the system should be set to match the voltage range of the analyzer output. In the WBEA network the standard is 5V full scale and is scaled to convert the output signal to the concentration range outlined in section 3. For serial or LAN connection there must be a station router in place and configurations made to the analyzer settings, the router, and the data logger. See the DAS operations manual for instructions on configuring these channels.
- The analyzer has the capability to output specific alarms or a general alarm via a contact closure. These outputs are connected to the digital input section of the DAS. See the DAS operations manual for instructions on configuring these channels
- The monitoring station temperature should be controlled within the range of 15 to 30°C. It is important to note that the analyzer will operate properly at any temperature within this range; however, the stability of the station temperature is most important.
- Within the vicinity of the station all products containing solvents and other sources of hydrocarbon must be avoided.
- Range Set – the typical range used for monitoring O_3 is 0 to 500 ppb. This is done as soon as the analyzer is powered up after installation. Refer to the operations manual for instructions on this procedure.

Operational and Maintenance Requirements

The following activities must be performed when operating a continuous automated UV photometric ozone analyzer in Alberta. All operational activities conducted at any ambient monitoring station must be documented in the Doc-It system. This allows other operators to access a history of the station if the regular technician is not available. The following documentation must be available to the operators on site: operational and maintenance manual(s), quality system manual and station site documentation.

Daily Requirements

Zero/Span Check – a zero/span cycle is required every day to verify the analyzer's performance. This involves diverting the sample flow of the analyzer so that the analyzer subsequently samples zero air for the zero cycle and air with a known amount of O_3 for the span cycle. These two sources are typically provided by internal systems. Zero is typically provided by pulling air through a charcoal canister, and span by pulling air from an internal Ozone generator. This cycle is normally controlled by the data system in the station, as it also flags the collected data as calibration and not sample data. The data system is programmed to close contacts that are connected to the zero and span contacts on the analyzer. Refer to the analyzer manual for more information.

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Analyzer Test Parameters

The analyzer monitors and displays test functions in order for the operator to monitor the performance of specific systems within the analyzer. These test parameters should be recorded digitally via DAS collection or documented on calibration reports.

Inlet Filter Change

The sample inlet filter is typically replaced when the monthly multipoint calibration is being done. The filter change is completed after the as found points have been completed and before the multipoint calibration is carried out. This is done to establish a reference prior to the removal of the filter.

Analyzer Maintenance

Preventative maintenance tasks should be completed on the analyzer on a periodic basis. These tasks are outlined in the operations manual. A strict regiment of these tasks should be adhered to as they are intended to fix a problem before it happens. Any maintenance must be recorded in the Doc-It system. This is also recorded in the instrument log that accompanies each instrument.

Multipoint Calibration

Multipoint calibrations are conducted on the O_3 analyzer to verify precision, accuracy and linearity of the instrument. This procedure must be completed after the analyzer has been installed following at least a 24 hour warm up period, prior to removal, and monthly to comply with Alberta Environment regulations. This procedure is also completed before and after any major maintenance to confirm the precision and accuracy after repairs.

Analyzer Audit

O_3 analyzers operating in Alberta are required to undergo an on-site audit once per year. This audit involves the Alberta Environment Audit Program staff visiting the site with the NIST traceable standards to verify the accuracy and linearity of the instrument.

Calibration Requirement

The calibration procedure for Ozone analyzers is similar to calibration of other continuous ambient air analyzers. This procedure involves generating a known amount of ozone, which is introduced to the analyzer to verify its performance. There are certain specifics to the Ozone calibration that are identified in this section. The main calibration procedure can be found in WBEA SOP-OPS-002 Dilution Calibration Procedure.

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- Calibration Equipment – Calibration equipment used to complete the Ozone analyzer calibration is the same as is used for the NO_2 calibration. A dilution calibrator with the capability of generating stable low level Ozone concentrations. The Ozone calibration is completed in conjunction with the NO_2 calibration as the Ozone concentration values are calculated from the GPT portion of the NO_2 calibration (specifically the calculated concentration of NO2 derived from the GPT). A zero air system is used to supply clean air for the calibrator. The system should supply zero air with less than 1.0 ppb of ozone, less than 1.0 ppb of NO_X and less than 1.0 ppb of organic compounds.
- Ozone Calculations – The generated Ozone concentrations used to reference the analyzers response are calculated from the GPT portion of the NO_2 calibration. From the NO_2 calibration, the calculated NO drop is equal to the Ozone concentration. The conditions used to calibrate the NO_2 analyzer must be recreated exactly for the Ozone calibration. The calculated NO drop values are used as the Ozone concentrations for the Ozone calibration.
- Calibration results must be graphed as indicated concentrations (C_i) versus calculated concentrations (C_c) from which the slope of the graph, the intercept and final correction co-efficient are calculated.
- The acceptance criteria are slope of 1.0, ±0.05, and intercept of ±3% full scale and a coefficient of correlation (CC) >0.995.
- A zero/span check cycle is run through the DAS following the calibration to verify the span values and to pick up and zero offset.
- A recorded trace of the instrument, response over time is required to demonstrate stability and accuracy.

Data Collection and Management

The analog output of the O_3 analyzers is typically wired to the analog input channels of the station Campbell's Scientific CR3000 data logger. This data recorded at 5 minute intervals and is then polled remotely via cellular modem. Alternatively the data can be polled digitally via the serial or Ethernet port, and can be accompanied by the diagnostic or meta-data information.

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Reference Documents

- Teledyne – Advanced Pollution Instrumentation (API), Inc Model 400E; API Model 400/400A Ozone Analyzers Operating Manual
- Thermo Environmental Instruments (TEI) Models 49, 49C Ozone Analyzers Operating Manual
- Canada Wide Standard (CWS) “Guidance Document on Achievement Determination-Canada Wide Standards for Particulate Matter and Ozone” 2000 and 2007 Amendments
- Methods of Air Sampling and Analysis, 3rd edition. . Lodge. 1991., *p.422*)
- “Technical Assistance Document for the Calibration of Ambient Ozone Monitors”EPA/600/4-79-057, September 1979, United States Environment Protection Agency, Research Triangle Park, NC 27711.

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