

Monitoring Parameter: Ozone (O₃)	Title: Standard Operating Procedure for the Continuous Measurement of Ambient O₃
Revision No: Draft Revision Date: 07 March, 2018	Reference No: SOP-04 Parent Document: Part B1 – B.C. Field Sampling Manual
<p>1. Introduction and Scope</p> <p>This Standard Operating Procedure (SOP) provides operating guidelines and instructions for the continuous ambient monitoring of Ozone (O₃) within the jurisdiction of British Columbia (B.C.).</p> <p>This SOP forms part of the B.C. Field Sampling Manual (BCFSM). Part B - Air and Air Emissions Testing, of the BCFSM provides additional information on Air Quality Monitoring that must be used in conjunction with the information provided in this SOP. Installation and maintenance of an O₃ analyzer within the provincial jurisdiction of B.C. must be carried out with consideration to Part B of the B.C. Field Sampling Manual, the analyzer manufacturer’s manual, and this document.</p>	
<p>2. Principle of the Method</p> <p>Selective Absorption of Ultraviolet (UV) Photometry</p> <p>The principle detection and quantification method deployed for ambient concentrations of Ozone (O₃) is selective UV absorption (at a wavelength of 254 nm) by O₃. The concentration of O₃ is determined using two steps of UV photometry, and the application of the Beer-Lambert Law.</p> <p>In the first step ozone is removed from the sample stream as it passes through an O₃ scrubber. The intensity of the UV rays in the ozone free environment is measured by the analyzer’s stabilized photo detector to provide a reference value. In the second step, the sample air bypasses the O₃ scrubber. Ozone present in the sample air absorbs UV in the 254 nm range and this reduction in UV rays is represented in the UV measurement provided by the photo detector. The Beer-Lambert Law shows that UV light absorption is proportional to the ray’s travel path, and the concentration of O₃. Using this relationship the concentration of ozone in the air sample can be determined.</p> <p>A more detailed discussion on the O₃ measurement principle is typically provided within the manufacturer’s operation manual.</p>	
<p>3. Interferences</p> <p>NO₂, SO₂, and VOCs</p> <p>Nitrogen dioxide (NO₂), sulphur dioxide (SO₂), and volatile organic compounds (VOCs) are known to influence O₃ measurement, however, in a typical urban environment the interference effect is reported to be negligible.</p> <p>H₂O, NO, Hg, and PAHs</p> <p>Other compounds that affect the measurement of O₃ are water (H₂O), Nitric Oxide (NO), and Polycyclic Aromatic Hydrocarbons (PAHs). Mercury vapour is a strong absorber of UV radiation at the 254 nm range and therefore O₃ cannot be measured using this method in the presence of mercury vapour.</p>	

Similarly, PAHs are a strong absorber of UV radiation at the 254 nm range, and at high concentrations, PAHs may interfere with the measurement.

Particulate Matter

The presence of particulate matter in an air sample is known to interfere with the measurement of Ozone. Particulate matter if present will absorb and scatter UV radiation. This can be minimized by installing a particle filter at the sample inlet (for analyzers that do not have an internal filter).

4. Precision and Accuracy

Air contaminant concentration measurements are affected by an instrument's precision and accuracy.

The precision of a measurement is generally considered to be the 'repeatability of the measurement'. This can be confirmed through zero and span checks, and multipoint checks/verifications.

The accuracy of the sensor is generally considered a measure of the 'deviation from true'. The accuracy of the sensor can be checked by performing a verification check against a certified reference standard photometer (see section 10 and 11). Accuracy can also be confirmed through span checks and calibrations.

5. Recommended Equipment and Apparatus

The following are commercially available O₃ analyzers suitable for use within the provincial jurisdiction of B.C.:

- Thermo Environmental Instruments (TEI) Models 49, 49C, 49i
- Serinus 10
- Teledyne API T400

This list does not necessarily exclude other commercially available O₃ analyzers, and analyzers recognized by the United States (US) Environmental Protection Agency's (EPA) Federal Reference and Equivalent Methods. In deed as technology advances, new analyzers will enter the market which may be suitable for use within the provincial jurisdiction of B.C. It is highly recommended however that you consult with the B.C. Ministry of Environment and Climate Change Strategy (ENV) if you intend to deploy O₃ analyzers not listed above. Regardless of the equipment deployed all analyzers should meet the specifications described within this document.

6. Measurement Range and Sensitivity

Typical commercially available O₃ analyzers can operate at a user selectable range of 0 ppb to 1000 ppb; for B.C. ENV monitoring purposes analyzers should be set to a range of 0 ppb to 500 ppb. Detection limits are determined by instrument type but are generally around 1 ppb.

Multipoint verifications and calibration should be conducted across a range of 2 ppb to 200 ppb.

7. Site Requirements

Monitoring site specifications should be developed to ensure that the data generated from the site satisfies the requirements of intended or established monitoring objectives. It is recommended that monitoring site requirements be established in consultation with the B.C. ENV to ensure that siting requirements are commensurate with monitoring objectives.

As a preliminary guideline site selection should consider and address: monitoring objectives, representativeness of the region, interference from the surrounding area, and monitoring location zone type (residential, commercial, industrial).

Refer to Section 2 of the Field Sampling Manual for further information on site selection.

8. Installation Requirements

Follow analyzer specific installation requirements provided in the analyzer manufacturer's manual. The installation should also conform to the following:

- The monitoring station's sampling inlet and manifold shall meet the requirements of the most recent version of the National Air Pollution Surveillance (NAPS) Program's *Monitoring and Quality Assurance/Quality Control Guidelines* Section 8.2 and Section 8.3.
- The ¼ inch diameter connection tubing from the manifold to the analyzer inlet must be made of Teflon or equivalent material for chemical inertness.
- All connectors and fittings in the sampling systems must be Teflon or stainless steel (connections should be Teflon-to-Teflon or steel-to-steel – no mixing of fittings at any connection point).
- A Teflon particulate filter meeting the instrument manufacturer's pore-size specifications unless the analyzer is equipped with a similar internal filter. The filter holder must be constructed of an inert material (e.g. Teflon, stainless steel).
- A data acquisition system (DAS) should be connected to the analyzer to record or download the measurement data from the analyzer. If an analog data logger is used, it must be set to match the voltage range of the analyzer, typically at 1 V or 10 V full scale. It must be ensured that the analog output matches the digital output displayed on the analyzer. The data logger must also record and monitor any alarm conditions of the analyzer.
- The analyzer must be placed in a temperature controlled, temperature stable enclosure. The enclosures temperature must be maintained between 20 °C to 30 °C.
- Remove any sources of solvents and volatile hydrocarbons from the vicinity of the station.

9. Operational Requirements

The following activities should be performed by the operator of a continuous automated O₃ analyzer.

Action	Time/Frequency	Description	Record Keeping
Analyzer Range Set Up	After installation	As per manufacturers operation manual. Monitoring range should be 0 ppb to 1000 ppb	Record in logbook, see example station installation record (Field Sampling Manual, Appendix 1)
Multipoint Verification	<ul style="list-style-type: none"> • After installation (or relocation) after a 24 h to 72 h warm up period; • After analyzer repairs/maintenance that may affect performance of the instrument; 	As per Section 11 of this SOP	Record in logbook, see example gas calibration activity record (Field Sampling Manual, Appendix 1)

	<ul style="list-style-type: none"> • When zero check exceeds ± 2.0 ppb; • When span drift is $\geq, \pm 10\%$ of reference value; • For new analyzers, after the first 3 months of operation • Bi-annually if span checks are conducted daily – or when any threshold above is reached (whichever happens first); • Quarterly if span checks are conducted less than daily – or when any threshold above is reached (whichever happens first). 			
Zero and Span Verification	Daily preferred, weekly minimum	As per manufacturers operation manual	Record in logbook, see example routine maintenance record (Field Sampling Manual, Appendix 1)	
Verify Operational Parameters	Each station visit	As per manufacturers operation manual		
Inlet Filter Change	Inspect monthly, change as required	As per manufacturers operation manual		
Analyzer Maintenance	As recommended by manufacturer or as required	As per manufacturers operation manual	Record in logbook	
Sample Path Inspection (Manifold to Analyzer)	Monthly	Where necessary replace with new lines, tighten loose connections, clean manifold if required	Record in logbook	

10. Zero and Span Checks

Zero and span checks are required to verify the analyzers performance between calibrations. These checks should be performed in accordance with Section 6 of the B.C. Field Sampling Manual and the manufacturer’s manual.

11. Multi-Point Verification and Calibration

Calibration should be performed in accordance with Section 6 of the B.C. Field Sampling Manual and the manufacturer’s manual.

12. References

National Air Pollution Surveillance (NAPS) Program. Monitoring and Quality Assurance/Quality Control Guidelines.

Alberta Environment (AENV) 2011. *Standard Operating Procedure for Measurement of Ozone in Ambient*

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EC 2004. *NAPS Network Quality Assurance and Quality Control Guidelines*. EC Environmental Protection Service Environmental Technology Advancement Directorate Analysis and Air Quality Division. Report No. AAQD 2004-1.

Thermo Fisher Scientific 2011. *Model 49i Instruction Manual UV Photometric O₃ Analyzer*.

United States (US) Environmental Protection Agency (EPA) 2013. *QA handbook for Air Pollution Measurement Systems Volume II Ambient Air Quality Monitoring Program*. US EPA Office of Air Quality Planning and Standards Air Quality Assessment Division.

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Approval

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