Monitoring Parameter: **Sulphur Dioxide (SO_2)**	Title: **Standard Operating Procedure for the Continuous Measurement of Ambient SO_2 DRAFT**
Revision No: Draft **Revision Date: 25 April, 2017**	**Reference No: SOP-06** **Parent Document: Part B1 – B.C. Field Sampling Manual**

1. Introduction and Scope

This Standard Operating Procedure (SOP) provides operating guidelines and instruction for the continuous ambient monitoring of Sulphur Dioxide (SO_2) within the provincial jurisdiction of British Columbia (B.C.).

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 SO_2 analyzer within the provincial jurisdiction of B.C. should be carried out with consideration to Part B of the B.C. Field Sampling Manual, the analyzer manufacturer's manual, and this document.

2. Document Control

This Standard Operating Procedure is a controlled document. Document control provides a measure of assurance that the specifications and guidance it provides are based on current information that has been scrutinized by a qualified reviewer/s. Controlled documents are reviewed within a five year life cycle. Please ensure that the revision date listed in the header of this document does not exceed five years.

This SOP and the B.C. Field Sampling Manual are available at: www2.gov.bc.ca.

3. Principle of the Measurement Method

Ultraviolet fluorescence

The principle detection and quantification method deployed for ambient concentrations of SO_2 involves ultraviolet (UV) fluorescence and a photomultiplier tube.

$$SO_2 + hv_1 \rightarrow excited\ state\ SO_2 \rightarrow SO_2 + hv_2$$

The concentration of SO_2 in a sample of ambient air is quantified as a measure of ultraviolet (UV) fluorescence absorbed by the SO_2 molecules in the sample. A bulb within the analyzer emits the UV rays which are absorbed by the SO_2 molecules at a wavelength of 214 nm. The absorption of UV rays causes the SO_2 molecules to transition to an excited state. As the excited state SO_2 molecules return to their normal state they release energy by emitting UV light at a wavelength of 330 nm. The SO_2 analyzer measures the amount of UV light present at a wavelength of 330 nm using a photo multiplier tube. The measurement of 330 nm UV rays is then used to quantify the concentration of SO_2.

A more detailed discussion on the SO_2 measurement principle is typically provided within the manufacturer's operation manual.

4. Interferences

As the principle method of measuring the concentration of SO_2 relies on the measurement of ultraviolet (UV) fluorescence, compounds that emit UV rays at similar wavelengths may, if present, interfere with the measurement of SO_2. Compounds such as Nitric Oxide (NO), hydrocarbons, Ozone (O_3), Carbon Dioxide (CO_2) and water (H_2O) emit UV rays at similar wavelengths and as such have the potential to interfere with SO_2 measurements.

Hydrocarbons
To minimize interference from hydrocarbons, SO_2 analyzers can be equipped with a hydrocarbon scrubber.

NO
The presence of NO compounds at sufficiently high concentrations can result in a detectable interference in SO_2 measurement. The use of optical filters can greatly reduce this interference by limiting the wavelength emitted by the UV bulb and the wavelength of the photomultiplier tube (PMT) to those specific to SO_2 absorption and emission. Greater interference can be observed when measuring trace levels of SO_2 when sufficiently high concentrations of NO are present in ambient air. If typical ambient levels of NO are known to be high relative to SO_2, particularly for trace level analyzers, it is recommended that the analyzer be tested for its degree of sensitivity to NO using span gas at concentrations of 600 ppb to 800 ppb NO.

O_3
Although current analyzers are equipped to reduce interference caused by O_3 it's important to recognize this potential interference. O_3 interferes with the measurement of SO_2, due to its absorption of a broad wavelength range of UV light. To counteract this interference the wavelength of the PMT is kept to a short light path.

Particulate Matter
The presence of particulate matter in an air sample may to interfere with SO_2 measurement. This can be minimized by using a particle filter of 5 µm pore size (for analyzers that do not have an internal filter). The filter must be made of an inert material such as Teflon and should be installed at the sample inlet.

Chemical Reactions
Chemical reactions between SO_2 and NO, CO_2, and H_2O are reported to have negligible interference.

5. 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 calibrations.

The accuracy of the sensor is generally considered to be a measure of the 'deviation from true'. The accuracy of a sensor can be evaluated and adjusted by performing a calibration against a certified sulphur dioxide calibration standard mixture (See sections 11 and 12 below). Accuracy can also be evaluated through span checks and calibrations.

6. Recommended Equipment and Apparatus
The following instruments are commercially available SO_2 analyzers deemed to be suitable for use within the provincial jurisdiction of B.C.:

- Thermo Environmental Instruments (TEI) Models 43i SO_2 Analyzers.
- Teledyne API T200
- Ecotech EC9850T

This list does not necessarily exclude other commercially available SO_2 analyzers, and analyzers recognized by 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 SO_2 analyzers not listed above. Regardless of the equipment deployed all analyzers must meet the specifications described within this document.

7. Measurement Range and Sensitivity

Typical commercially available SO_2 analyzers can operate at a user selectable range of 0 ppb to 1000 ppb. For B.C. ENV monitoring purposes the range should be set at 0 ppb to 200 ppb or 0 ppb to 500 ppb. In areas where high SO_2 concentrations are likely consult with B.C. ENV to establish an appropriate range to capture peak ambient concentrations.

Detection limits are determined by instrument type but are generally around 0.3 ppb.

8. Site Requirements

Monitoring site requirements 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 the monitoring objectives.

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

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

9. Installation Requirements

Follow analyzer specific installation requirements discussed 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.
- All connection tubing, connectors and fittings from the manifold to the analyzer inlet must be made of Teflon or a material of equivalent chemical inertness.
- A Teflon particulate filter capable of removing at least 99% of 1 micron and larger particles must be placed in the sampling line upstream of the analyzer, unless the analyzer is equipped with a similar internal filter. The filter holder should be constructed of an inert material (e.g. Teflon, stainless steel).
- A data acquisition system (data logger) 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. 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 enclosure's temperature must be maintained between 20 °C to 30 °C.
- Remove any sources of solvents and volatile hydrocarbons from the vicinity of the station.

10. Operational Requirements

The following activities should be performed by the operator of a continuous automated SO_2 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 500 ppb	Record in logbook, see example station installation record (B.C. Field Sampling Manual, Appendix 1)
Multipoint Verification	• After installation (or relocation) following a 24 hour warm up period; • For new analyzers, after the first 3 months of operation; • After analyzer repairs/maintenance that may have affected the performance of the instrument; • When the span check is less than or is equal to ± 10 % of reference value; • When the zero check exceeds ± 1.0 ppb; • Quarterly required if using weekly zero/span checks. A maximum 6 month interval is permissible if using daily zero/span checks.	As per Section 11 of this SOP	Record in logbook, see example gas calibration activity record (B.C. Field Sampling Manual, Appendix 1)
Zero and Span Verification	Daily preferred, weekly minimum	As per manufacturers operation manual	Record in logbook, see example routine maintenance record (B.C. 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 (Probe to Analyzer)	Monthly	Where necessary replace with new lines, tighten loose	Record in logbook

		connections, clean manifold as required	

11. 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.

12. 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 SO_2 by SO_2 Fluorescence*. AENV Air Monitoring and Audit Centre.

AENV 2011. *Standard Operating Procedure for Dilution Calibrations*. AENV Air Monitoring and Audit Centre.

Environment Canada (EC) 2010. *Continuous Measurement of Sulphur Dioxide (SO_2) in Ambient Air by UV Fluorescence*. EC National Air Pollution Surveillance (NAPS) Operations Unit.

Thermo Fisher Scientific 2015. *Model 43i Instruction Manual Pulsed Fluorescence SO_2 Analyzer*.

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.

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