Monitoring Parameter: **Methane and Non-Methane Hydrocarbons**	Title: **Standard Operating Procedure for the Non-Continuous Measurement of Ambient Methane and Non-Methane Hydrocarbons Using Gas Chromatography**
Revision No: Draft **Revision Date: 09 April, 2018**	**Reference No: SOP-10** **Parent Document: Part B1 – B.C. Field Sampling Manual**

1. Introduction and Scope

This Standard Operating Procedure (SOP) provides operating guidelines and instructions for the continuous ambient monitoring of Methane and Non-Methane Hydrocarbons (NMHC), 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 a Methane/NMHC analyzer within the provincial jurisdiction of B.C. should be carried out with consideration to Part B of the BCFSM, 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

Gas Chromatography (GC)

The principle detection and quantification method deployed for monitoring Methane and Non-Methane Hydrocarbons (NMHC) in ambient air is gas chromatography (GC). Methane/NMHC analyzers use a semi-continuous collection and analysis sequence that draws air samples into a separation column where it is pushed by an inert carrier gas into a flame ionization detector (FID). Due to the differences in molecular weight and volatility the sample's various gas components are separated based on retention time.

Retention time is described as the time it takes for a component to travel though and emerge from the column. Methane has a lower molecular weight and higher volatility than other hydrocarbons which results in a lower retention time. For this reason methane is the first compound to emerge from the separation column. The Methane is then directed to a flame ionization detector (FID). The signal produced by the FID is converted to a methane concentration by comparing the response to a known concentration of a methane standard. Non-methane hydrocarbons emerging later from the separation column produce an FID signal which is converted to an NMHC concentration using comparisons with a known concentration of a propane standard. After the NMHC measurement is complete, the analyzer initiates the next sample analysis.

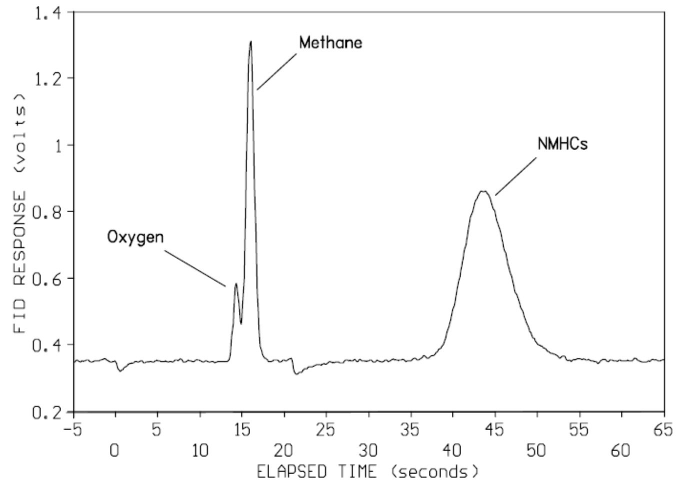

Figure reference: Thermo Scientific, 2012

A typical gas chromatogram from a Thermo Scientific Model 55i Analyzer using 2 ppm each of methane and propane (a NMHC) is shown in the figure above.

4. Interferences

Particulate Matter

The presence of particulate matter in air samples may interfere with Methane/NMHC analyzer response. Interference by particulate matter can be minimized by using a particle filter at the sample inlet. The filter must have a 2 µm diameter pore size and be made of an inert material such as Teflon.

5. Precision and Accuracy

The precision of an analysis 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 checked by performing calibrations against a certified calibration standard mixture (See Sections 11 and 12). Accuracy can also be confirmed through periodic span checks and multipoint checks/calibrations.

6. Recommended Equipment and Apparatus

The following are common commercially available methane/NMHC analyzers suitable for use within the provincial jurisdiction of B.C.:

- Thermo Scientific Direct Methane, Non-Methane Hydrocarbon Analyzer, Model 55i
- Synspec GC's Alpha 115

This list does not necessarily exclude other commercially available Methane/NMHC analyzers, and analyzers recognized by the United States (US) Environmental Protection Agency (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 Methane/NMHC analyzers that are not listed above. Regardless of the instrument deployed, all analyzers should meet the specifications described within this document.

7. Measurement Range and Sensitivity

Typical commercially available Methane/NMHC analyzers operate at user selectable ranges between 0 ppm and 5000 ppm; for B.C. ENV monitoring purposes analyzers should be set to a range of 0 ppm to 20 ppm for Methane/NMHC.

The detection limit is determined by instrument type but is generally around 0.05 ppm.

8. Site Requirements

Monitoring site specifications should be developed to ensure that the data obtained from the site satisfies the requirements of intended or established monitoring objectives. It is highly 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 zone type (residential, commercial, industrial) of the monitoring location.

Refer to Section XX of the BCFSM for further information on site selection.

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.
- The ¼ inch diameter connection tubing from the manifold to the analyzer inlet must be made of Teflon or equivalent material for chemical inertness.
- A Teflon particulate filter capable of removing at least 99% of 1 µm diameter 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 ('DAS' or '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. 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 weather resistant enclosure that is vented, heated and cooled to maintain a stable temperature preferably in the range of 20 °C and 30 °C but must be capable of maintaining the operating temperature range specified by the manufacturer. Enclosure temperatures should not deviate by more than 2 °C over a one hour period.

10. Operational Requirements

The following activities should be performed by the operator of a continuous automated Methane/NMHC analyzer.

Action	Time/Frequency	Description	Record Keeping
Analyzer Range Set Up	After installation	As per manufacturers operation manual. Monitoring range should be 0 ppm to 20 ppm.	Record in logbook, see example station installation record (BCFSM, Appendix XX)
Multipoint Verification	• After installation (or relocation) following a 24 h to 72 h warm up period; • After analyzer repairs/maintenance that may affect performance of the instrument; • When zero check exceeds ± 0.1ppm; • When span drift is ≥ ± 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).	As per Section 12 of this SOP.	Record in logbook, see example gas calibration activity record (BCFSM, Appendix XX)
Zero and Span Verification	Daily preferred, weekly minimum	As per manufacturers operation manual.	Record in logbook, see example routine maintenance record (BCFSM, Appendix XX)
Verify Operational Parameters	Each monitor station visit	As per manufacturers operation manual.	
Check Support Gas Pressures	Each monitor station visit	Check gas cylinder pressures and replace if they drop below 500 psi.	
Inlet Filter Change	Inspect monthly, change as required	As per manufacturers operation manual. A filter change can affect flow and pressure so a verification or full calibration is required.	

Analyzer Maintenance	As recommended by manufacturer or as required	As per manufacturers operation manual.	Record in logbook
Sample Path Inspection (Probe to Analyzer)	Each monitor station visit	Where necessary replace with new lines, tighten loose connections, clean manifold if required. Any alteration to the sample pathway should be accompanied by verification or full calibration.	Record in logbook

11. Zero and Span Checks

Zero and span checks are required to verify analyzer performance between calibrations. These checks should be performed in accordance with Section XX of the BCFSM.

12. Calibration

Calibration should be performed in accordance with Section XX of the BCFSM and following the manufacturer's manual. Methane/NMHC analyzers are typically calibrated using the dilution method

13. References

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

Alberta Environment (AENV) 2011. *Standard Operating Procedure for Measurement of Methane/Non-Methane Hydrocarbons Using FID Detection.* AENV Air Monitoring and Audit Centre.

CARB 2002. *Standard Operating Procedure for the Determination of non-Methane Organic Compounds in Ambient Air by Gas Chromatography Using Dual Capillary Columns and Flame Ionization Detection*. Northern Laboratory Branch Monitoring and Laboratory Division.

Synspec 2010. *Synspec GC's Alpha 115 and Alpha 116 Methane/Total Non Methane HydroCarbons Operator manual*.

Thermo Scientific 2012. Model 55i *Instruction Manual Direct Methane, Non-Methane Hydrocarbon Analyzer*.

United States Environmental Protection Agency (US 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.

Wood Buffalo Environmental Association (WBEA) 2013. Procedures for Operating Continuous Methane/Non-Methane Hydrocarbon Analyzers.

Revision History: 0.0 (New document)

Approval