



## 1.0 Introduction

The measurement of methane and non-methane hydrocarbons is based on the science of gas chromatography (GC) and utilizes a proprietary column system developed specially for this application. Unlike instruments that measure only methane and total hydrocarbons, the back-flush GC method provides a direct measurement of non-methane concentrations. This allows accurate and precise measurement of low levels of non-methane hydrocarbons (NMHC), even in the presence of methane at much higher concentrations.

The methane, non-methane hydrocarbon analyzer is an automated batch analyzer which repeatedly collects and analyzes small amounts of the sample stream drawn in by the pump. Central to the instrument's operation is an eight port, two position, rotary valve which is used to introduce the gas sample into the analyzer and to control the flow of gases through the chromatography column.

Each sample run takes approximately 70 seconds, the first peak is the methane, and the second non-methane. The combined concentration yields the total hydrocarbon result.

## 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 methane and non-methane hydrocarbon concentrations in ambient air

This method is capable of measurement updates at a rate of once every minute. This method captures and records THC, methane and non-methane 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 THC concentrations in ambient air in the range of 0.1 parts per million (ppm) to 40 parts per million (ppm). This method is applicable to the measurement of Methane concentrations in ambient air in the range of 0.1 parts per million (ppm) to 20 parts per million (ppm). This method is applicable to the measurement of Non-Methane (NMHC) concentrations in ambient air in the range of 0.1 parts per million (ppm) to 20 parts per million (ppm).

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 operating manual.

#### 4.1 Reporting Detection Limits

The methane, non-methane hydrocarbon analyzers used in this method are commercially available models. The measurement range is user selectable at ranges between 0 to 10,000 parts per million by volume (ppm). The typical range selection used in Alberta is 0 to 20 ppm for both methane and non-methane, and 0 to 40 ppm for total hydrocarbons.

Data generated from these analyzers are reported to the nearest 0.01ppm

### 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 any hydrocarbons, 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.
- Within the vicinity of the station all products containing solvents and other sources of hydrocarbon will be avoided.
- 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. It includes that THC channel, Methane (CH<sub>4</sub>) channel, and NMHC channel.
- Support gas pressures will be checked every station visit. If a gas is changed a calibration is not required, however if the daily span gas is changed a zero and span must be done in order to determine the new expected value for the daily span, and entered in to the calibration program in the logger.

## 6.0 Calibration Procedure

Below is the procedure used to calibrate the analyzer for the monthly multi-point calibration.

NOTE - 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.

- a. Initiate flow of a zero-air gas to the analyzer. Record the "Diluent and Cal Gas" flow rates.
- 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 0.00.
- d. After the adjusted monitor reading has stabilized for 20 minutes, record the resultant adjusted zero reading as "adjusted zero".
- e. Initiate a flow of a known gas between 50% and 80% of the full scale to the analyzer. Record the "Diluent Flow Rate" and "Cal Gas Flow Rate". Determine the Calculated concentration (CC) (refer to 8.1-a).
- 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-b). 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 8.1b). Correction factor must be as close to 1.000 as possible.
  - h. Initiate a flow of a known gas between 25% and 40% of the full scale range. After the monitor reading has stabilized for 20 minutes, record the resultant instrument reading. Calculate the correction factor (CF) (refer to 8.1-b). Correction factor must be 0.95 to 1.05.
  - i. Initiate a flow of a known gas between 10% and 20% of the full scale range. After the monitor reading has stabilized for 20 minutes, record the resultant instrument reading. Calculate the correction factor (CF) (refer to 8.1-b). 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.

## 7.0 Quality Control Requirements

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

<b>Slope</b>	<b>0.85 to 1.15</b>
<b>Intercept</b>	<b>&lt; 3 % of full scale</b>
<b>Correlation Coefficient</b>	<b>&gt;0.995</b>

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. Methane Calculated Concentration (C.C.)

$$\text{C.C.} = \frac{(\text{Source Gas Flow Rate} \times \text{Cal Gas concentration})}{(\text{Source Gas Flow rate} + \text{Dilution Air Flow Rate})} \times 1000$$

Unit: ppm or ppb

b. Non-Methane Calculated Concentration (C.C.)

$$\text{C.C.} = \frac{(\text{Source Gas Flow Rate} \times (\text{Cal Gas concentration} \times 2.75))}{(\text{Source Gas Flow rate} + \text{Dilution Air Flow Rate})} \times 1000$$

Unit: ppm or ppb

c. Total Hydrocarbon Calculated Concentration (C.C.)

$$\text{C.C.} = \frac{(\text{Source Gas Flow Rate} \times ((\text{methane bottle value}) + (\text{propane bottle value concentration} \times 2.75))}{(\text{Source Gas Flow rate} + \text{Dilution Air Flow Rate})} \times 1000$$

Unit: ppm or ppb



d. Correction Factor (C.F.)

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

Unit: None

e. 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: %

f. Methane/Propane Mixture Concentration (C)

$$C = C_{\text{propane}} \times 2.75 + C_{\text{methane}}$$

Unit: ppm



## 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

Field service reports will track:

- Date of the calibration
- Consumables required
- Maintenance performed
- Time required
- Calibration anomalies and explanation