



Title: Standard Operating Procedure for Measurement of Methane/Non-Methane Hydrocarbons Using FID Detection		
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1. INTRODUCTION AND SCOPE

To obtain timely data for the purpose of air quality assessment, air quality trend reporting, and to meet the requirements for inclusion of the data in provincial and national air quality databases, a continuous method of analyzing Non Methane Hydrocarbons (NMHC) concentrations in ambient air is used. This method is capable of measurement updates at a rate of once every five minutes or faster. Readings from instruments of this method enables the calculation of hourly averaged concentrations of Total Hydrocarbons THC, Methane CH₄ and Non-methane Hydrocarbons NMHC. Commercially available NMHC analyzers are used in the method.

This method is applicable to the measurement of NMHC concentrations in ambient air in the range of 0.1 parts per million (ppm) to 50.0 parts per million (ppm).

This method adheres to the requirements of the current Air Monitoring Directive (AMD) 1989 by Alberta Environment. In some cases the limits and specifications exceed the requirements of the current AMD. 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. Information used to write this procedure was also taken from sources identified in the reference section.

2. PRINCIPLE OF THE METHOD

NMHC analyzers detect methane and non-methane hydrocarbon gases through the science of gas chromatography and utilizes a column system and flame ionization detector specifically designed for this application. A basic understanding of chromatographic principals will be helpful for the installation and troubleshooting of the analyzer.

This analyzer is an automated batch analyzer that repeatedly collects and analyzes small amounts of the sample stream. The sample is drawn into the analyzer using a pump system. The system is based around an 8-port, two position rotary valve, which supplies sample gas to the analyzer and the column (see figure 2.0).

There are two valve positions or modes, which are referred to as the “**Inject**” and “**Backflush**”. The cycle starts with the **Backflush** mode. The sample is drawn into the sample loop (a coil of empty tubing) (see Figure 2.1). The rotary valve now switches to the **INJECT** position (see Figure 2.1). The valve connects the sample loop to the column and the sample is pushed through the column by the carrier gas. Since the methane component of the gas is lighter (low molecular weight), the methane moves

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quicker through the column and goes out the column through the rotary valve to the flame ionization detector (FID) for analysis. Once the methane has been detected by the FID, the rotary valve then reverses, returning to the **BACKFLUSH** mode. The heavy hydrocarbons that are left in the column are now pushed in the reverse direction by the carrier gas through the rotary valve to the FID for analysis. This completes the sample gas cycle. Figure 2.2 shows a typical chromatogram as seen with calibration gas being injected into the analyzer. The graph is showing Volts (vertical) and Time (horizontal) and is connected to the FID output of the analyzer. Calibration gases suggested by the manufacturer are methane and propane (non-methane). The time required for the analysis of one sample is about 70 seconds. When you are only interested in hourly averages, it is recommended that you set the cycle time to about 224 seconds to extend the life of the rotary valve.

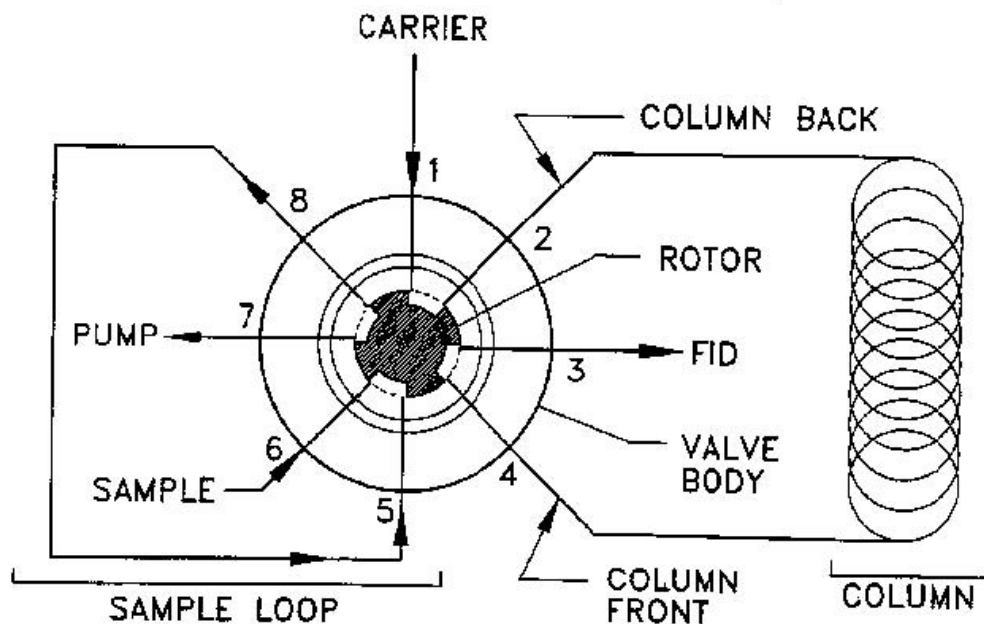


Figure 2.0: Rotary Valve

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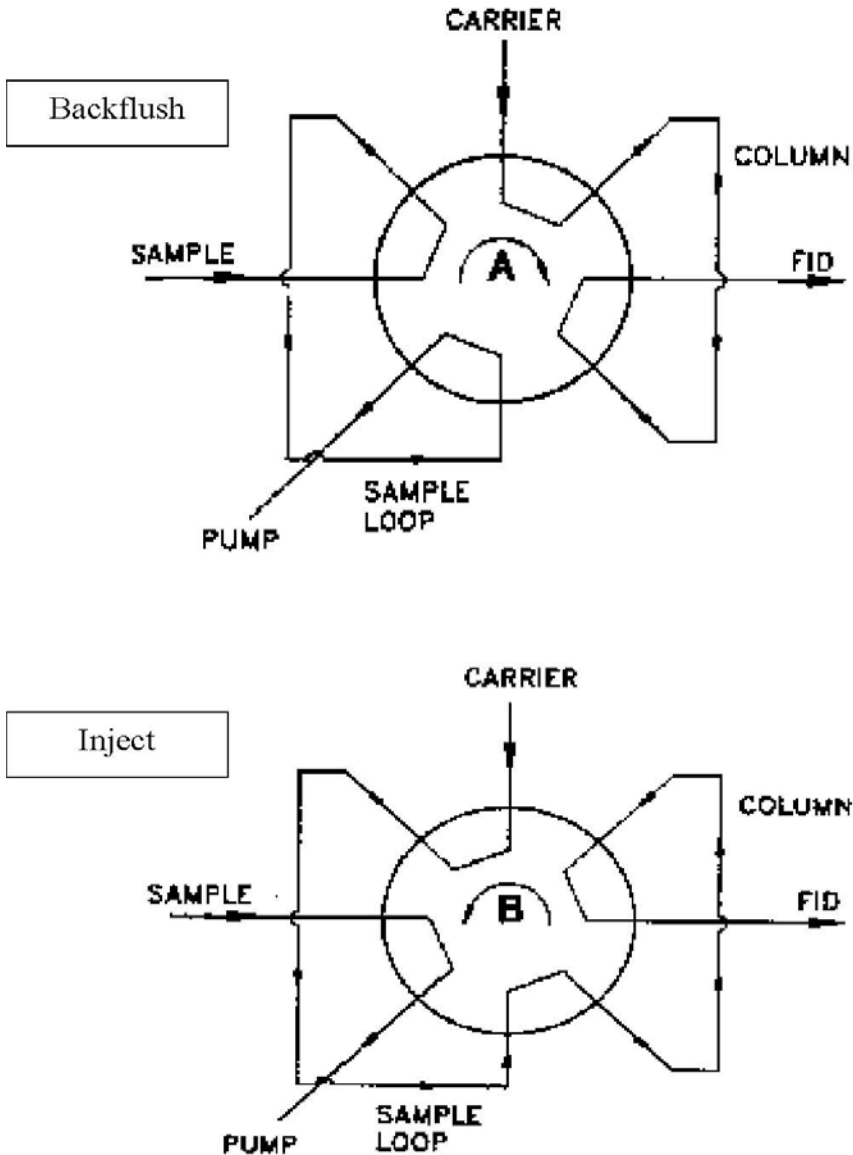


Figure 2.1: Backflush and Inject Positions

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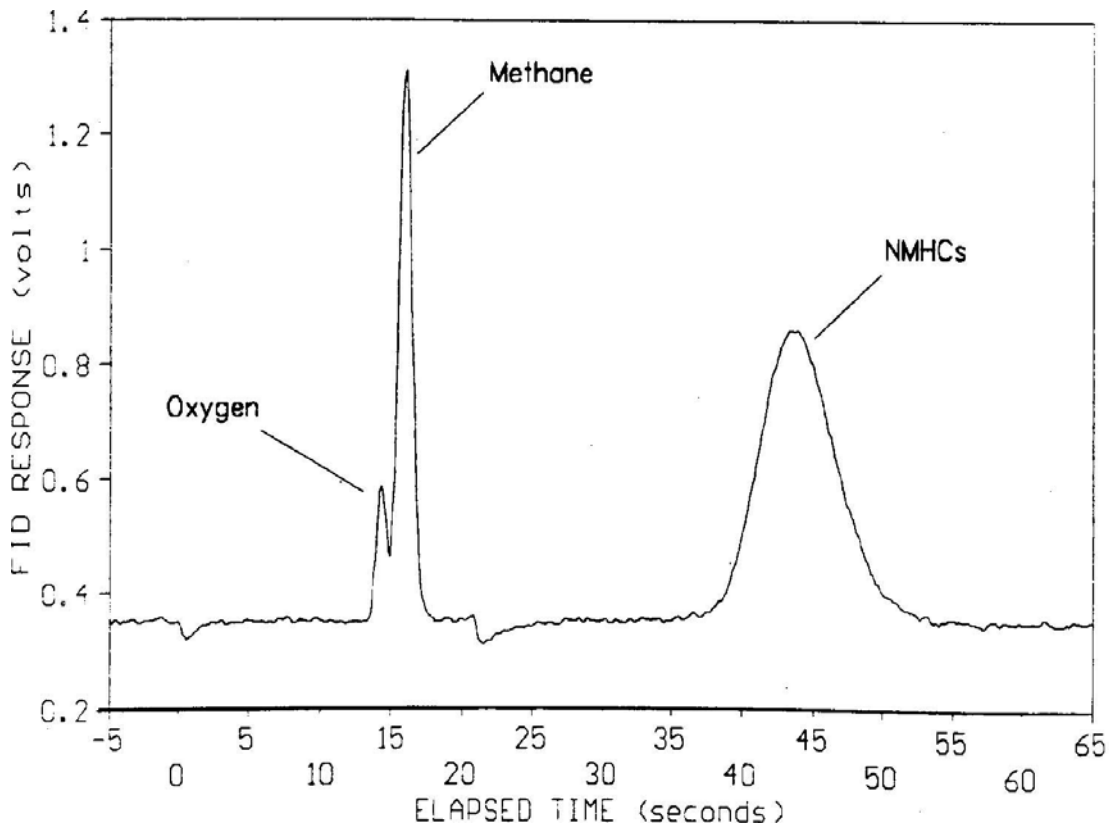


Figure 2.2: Backflush and Inject Positions

3. MEASUREMENT RANGE AND SENSITIVITY

The NMHC analyzers used in this method are commercially available models. The measurement range is user selectable at ranges between 0 to 200 parts per million by volume (ppm). The typical range selection used in Alberta is 0 to 40ppm for THC and 0 to 20 ppm for CH₄ and NMHC.

The detection limit of the analyzer is specified by the manufacturer. Generally it is at the 20 ppb for CH₄ and 50 ppb for NMHC as Propane.



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4. EQUIPMENT AND APPARATUS

The following are available commercial analyzers suitable for used in this method and are currently in use in the AENV network:

- Thermo Environmental Instruments (TEI) Model 55CLT NMHC Analyzer

This list does not exclude the use of other equipment that has received the USEPA Reference and Equivalent Method designation.

5. INTERFERENCES

The system is GC based, any compounds detectable by the FID are typically retained on the column and then flushed off the column during the backflush cycle.

Particulate matter may interfere with analyzer response. This problem is normally eliminated by using a particle filter of 2.0µm pore size made of inert material, such as Teflon, at the sample inlet of the instrument.

6. 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 spans checks and monthly calibrations. See section 9.0 in this document for information on daily 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 transfer standards from the National Institute of Standards and Technology (NIST). As with precision, accuracy is confirmed by the daily and monthly calibration checks. Refer to the sections identified above for further information on accuracy relating to calibration and audit procedures.

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7. SITE REQUIREMENTS

Site location for NMHC monitoring should be determined according to the intended application of the monitoring data. Detailed requirements for selection of sites for monitoring ambient NMHC can be found in Air Monitoring Directive

8. INSTALLATION REQUIREMENTS

All the installation requirements are specified by the manufacturer in the installation procedures of the manual. General requirements listed below must also be followed.

- 8.1 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.
- 8.2 A Teflon or glass fibre particulate filter 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, stainless steel or delrin.
- 8.3 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 DAS system should be set to match the voltage range of the analyzer output. Generally this is 1V or 10V full scale.
- 8.4 Connection of Status line to the logger should be mentioned here as well to monitor any alarm conditions.
- 8.5 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.

9. OPERATIONAL REQUIREMENTS

The following activities must be performed when operating a continuous automated NMHC analyzer in Alberta. All operational activities conducted at any ambient



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monitoring station, must be documented in the station logbook, and/or station checklists. 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), and station site documentation.

9.1 Set Up

Range Set – the typical range used for monitoring NMHC and CH₄ is 0 to 20 ppm 0 to 40 ppm for THC. This is done as soon as the analyzer is powered up after installation. Refer to the operations manual for instructions on this procedure. Setup configuration is recorded and kept with the instrument.

9.2 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 CH₄ and C₃H₈ for the span cycle. The zero source is typically provided by a zero air system consisting of a compressor, air dryer and a high temperature oxidizer for removal of hydrocarbons or a cylinder of Zero Air and span by a cylinder of CH₄/C₃H₈ in the appropriate range. This cycle is normally controlled by the data system DAS in the station, as it also flags the collected data as calibration and not sample data. The DAS 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. It is recommended to perform the zero check cycle last to reduce the time required for the instrument to return to ambient readings

9.3 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 monitored on a weekly basis and recorded on a site / instrument checklist. A variety of support gasses (described in section 9.2) are also required for the operation of these analyzers. Pressures of these cylinders should be monitored routinely so that cylinders are changed before they run empty. A good "rule of thumb" is to change the cylinders once they drop below 500 psi. (see appendix A) for an example of a station checklist.



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9.4 Inlet Filter Change

The sample inlet filter is typically replaced when the monthly multipoint calibration is being done. This should not occur until the as found points have been completed to rule out any interference. If the filter has visible particulate on it, change the filter with a new Teflon filter. Filters are changed out monthly before each calibration.

9.4 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 station log book and a record kept with the instrument documentation.

9.5 Multipoint Calibration

Multipoint calibrations are conducted on the NMHC 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, after any repairs or maintenance has taken place which may affect the performance of the instrument and monthly to comply with Alberta Environment regulations. Calibration procedures specific to the NMHC analyzer are found in section 10 of this document.

9.6 Analyzer Audit

NMHC 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.

10. CALIBRATION

The calibration procedure for NMHC analyzers is similar to calibration of other continuous ambient air analyzers. This procedure involves generating a known amount of $\text{CH}_4/\text{C}_3\text{H}_8$, which is introduced to the analyzer to verify its performance. There are certain specifics to the NMHC calibration that are identified in this section.

10.1 Calibration Equipment – NMHC analyzers are typically calibrated using the dilution method.

---THIS DOCUMENT MUST NOT BE PHOTOCOPIED---

Additional copies are available from the Air Monitoring Manager or designate

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- 10.2 Referring to the calibration procedure SOP 11 "SOP for Dilution Calibrations", calculate the slope and intercept of the 4 data points for all three parameters, CH₄, NMH & THC, against the calibrator values using linear regression analysis. The acceptance criteria are slope of 1.0±0.1 and intercept of +/- 3% full scale and a coefficient of correlation (CC) >0.998.
- 10.3 Analyzer is adjusted for the upscale reading of 1:1 at the highest scale point in the calibration. Slope and intercept corrections are not performed.
- 10.4 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.

11. APPLICABLE DOCUMENTS

- **EM-023a** Thermo Environmental Instruments (TEI) Model 55CTL NMHC Analyzer Operating Manual

12. LITERATURE REFERENCES

- State of California Air Resources Board (CARB) Method Volume II Standard Operating Procedures for Air Quality Monitoring Appendix AK dated June 2000
- State of California Air Resources Board (CARB) Method Volume II Standard Operating Procedures for Air Quality Monitoring Appendix J dated December 1995

13. REVISION HISTORY

Revision 0 (new document)

Revision 1.0 January 17, 2011 SOP reference in Section 10.2, other grammatical changes

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14. APPROVAL



Approved by: Harry Benders
Title: Air Monitoring Team Leader

Date: January 17, 2011